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Liquid−Liquid Equilibrium of (Water + Acetone) with Cumene or α-Methylstyrene or Phenol at Temperatures of (323.15 and 333.15) K

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We measured the liquid−liquid equilibrium and obtained the tie lines for the ternary systems of (water + acetone) and either cumene or α-methylstyrene or phenol at two temperatures of (323.15 and 333.15) K, at a pressure of 0.1 MPa. The NRTL model and the UNIQUAC model were fit to the experimental results in order to obtain interaction parameters for the components. The standard deviations of the calculated values from the experimental results were in the range (0.0026 to 0.0081). The UNIFAC model, based on group contribution, was also employed to describe the equilibrium conditions. For this model, the standard deviations were in the range (0.015 to 0.079) for these mixtures.

Introduction

Phenol is an important petrochemical feedstock, widely used to produce resins. It is produced by liquid-phase oxidation of cumene followed by the catalytic decomposition of the cumene hydroperoxide, which generates phenol and acetone. Besides water and α-methylstyrene, the reaction byproduct is α-methylstyrene and may be converted to cumene by hydrogenation. The mixture of products and byproducts is then separated by distillation and settling. The partial solubility of the organic compounds in water may prompt the appearance of two liquid phases in equilibrium, which jeopardize the aforementioned separation processes. Therefore, it is important to know equilibrium conditions regarding the mentioned system, which might involve liquid(s) and vapor phases. Thermodynamics allows the representation of any equilibrium form using data for another equilibrium form. However, this may not always provide a satisfactory prediction. Liquid + liquid equilibrium data are preferred over either liquid + vapor or liquid + liquid + vapor equilibrium data because these are more expensive to obtain and often of lower accuracy.[1]

Liquid + liquid equilibrium (LLE) data for (water + acetone + cumene) at temperatures of (323.15 and 333.15) K have been reported by Broglio.[1] Guttman and Wilczura[2] obtained binodal curves for (water + acetone + phenol) at temperatures between (323.15 and 333.15) K. Data for binary mixtures are available only for (water + phenol) that were reported by Gonzales et al.[3] There is no LLE data reported for (water + acetone + α-methylstyrene).

In this work, we obtained LLE data for the (water + acetone + cumene). (water + acetone + α-methylstyrene), and (water + acetone + phenol) systems at temperatures of (323.15 and 333.15) K at a pressure of 0.1 MPa. These systems have unique characteristics, such as the high volatility of acetone and the associative effect promoted by phenol, which challenges the experimental part. The NRTL model[4] and the UNIQUAC model[5] were fitted to the experimental results through new interaction parameters. The UNIFAC model,[6] based on group contribution, was also used to describe the LLE results.

Experimental Section

Materials. Ethanol (Chemical Abstracts Service Registry No. (CASRN) 64-17-5), used for chromatography, with a mole fraction purity of 0.995 was supplied by Merck. Phenol (hydroxybenzene, CASRN 108-95-2), cumene (1-methylethylbenzene, CASRN 98-82-8), and α-methylstyrene (1-methylethenylbenzene, CASRN 98-83-9), with mole fraction purities of 0.995 pure, were supplied by Rhodia (Paulinia, SP, Brazil). The chemicals were used without further purification. Deionized distilled water was used in all experiments.

Apparatus and Procedure. The investigation was carried out with glass equilibrium cells fitted with a heating jacket to control the temperature. The cells were sealed at a pressure of 0.1 MPa. The circulating water was kept at the desired temperature (with an uncertainty of ± 0.1 K) by a thermostatic bath (MLW, model MK70). The internal volume of the cells was 65 cm^3. Each cell had two sampling ports that were sealed with silicone, through which the phases were sampled. A thermometer was placed in the cell through a sealed hole on the cell atop. Broglio[1] employed a condenser to avoid loss of vaporized material; unfortunately, the condensed material returned to the cell and disturbed the equilibrium. Because of this, we decided not to use the condenser. A magnetic agitator was used to homogenize the system for 8 h. After a settling period of 12 h, the samples were collected with gastight syringe (Hamilton) and subsequently injected in vials containing ethanol, used both as solvent and internal standard. These times were the same and adequate for all systems, regardless of temperature and composition.

Analyses. Analyses were carried out in a gas chromatograph (Varian, model 3440cx) equipped with a flame ionization detector (FID) and a Carbowax 20 M packed column measuring 3 m long and $^1/_8$ in. outside diameter on Chromosorb W (80-100 mesh) to determine the concentrations of acetone, cumene, α-methylstyrene, and phenol. Water concentration was obtained by mass balance, using an analytical balance (Mettler H31HR) with ± 0.1 mg precision. A nitrogen carrier gas was used at a flow rate of 0.5 $cm^3 \cdot s^{-1}$. The quantitative method used ethanol as the internal standard due to its solubility, low toxicity, and low cost. The injector temperature was kept at 453.15 K, while the column was heated at temperatures between (383.15

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Table 1. Experimental LLE Results (mass fraction) for the System Water (1) + Acetone (2) + Cumene (3)

323.15 K				333.15 K			
aqueous phase		organic phase		aqueous phase		organic phase	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
0.9747	0.0253	0.0000	0.0189	0.9197	0.0801	0.0000	0.0698
0.9156	0.0843	0.0000	0.0665	0.9138	0.0860	0.0000	0.0725
0.9097	0.0901	0.0000	0.0710	0.8354	0.1642	0.0000	0.1514
0.8487	0.1511	0.0000	0.1239	0.8567	0.1430	0.0000	0.1304
0.8577	0.1421	0.0147	0.1225	0.8159	0.1836	0.0000	0.1782
0.8087	0.1908	0.0033	0.1710	0.8173	0.1821	0.0000	0.1740
0.7066	0.2916	0.0146	0.2945	0.7694	0.2298	0.0000	0.2329
0.5902	0.4044	0.0377	0.4396	0.7646	0.2345	0.0000	0.2361
				0.5996	0.3947	0.0362	0.4489
				0.6015	0.3930	0.0264	0.4525
				0.6052	0.3892	0.0288	0.4507

Table 2. Experimental LLE Results (mass fraction) for the System Water (1) + Acetone (2) + Phenol (3)

323.15 K				333.15 K			
aqueous phase		organic phase		aqueous phase		organic phase	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
0.9005	0.0309	0.2248	0.1469	0.8827	0.0337	0.2308	0.1456
0.8992	0.0305	0.2010	0.1472	0.8823	0.0305	0.2204	0.1332
0.8974	0.0284	0.2018	0.1392	0.8805	0.0161	0.2755	0.0737
0.8967	0.0147	0.2553	0.0782	0.8793	0.0472	0.2138	0.1901
0.8933	0.0448	0.1953	0.1958	0.8765	0.0341	0.2197	0.1427
0.8915	0.0460	0.1896	0.2012	0.8702	0.0580	0.2013	0.2183
0.8853	0.0544	0.1806	0.2253	0.8640	0.0693	0.1901	0.2478
0.8773	0.0667	0.1684	0.2552	0.8530	0.0834	0.2076	0.2743
0.8691	0.0776	0.1805	0.2732	0.8130	0.1227	0.2068	0.3310
0.8318	0.1160	0.1839	0.3341	0.7919	0.1411	0.2199	0.3483
0.8187	0.1278	0.1802	0.3540	0.7965	0.1350	0.2154	0.3429
0.8139	0.1345	0.2061	0.3487				

Table 3. Experimental LLE Results (mass fraction) for the System Water (1) + Acetone (2) + ∝-Methylstyrene (3)

323.15 K				333.15 K			
aqueous phase		organic phase		aqueous phase		organic phase	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
0.7657	0.2331	0.0107	0.2490	0.7733	0.2253	0.0231	0.2514
0.6985	0.2991	0.0192	0.3413	0.7160	0.2814	0.0317	0.3358
0.6942	0.3031	0.0372	0.3430	0.7129	0.2845	0.0354	0.3333
0.6640	0.3323	0.0366	0.3780	0.6804	0.3157	0.0280	0.3883
0.6614	0.3347	0.0334	0.3907	0.6715	0.3242	0.0305	0.3925
0.5990	0.3942	0.0226	0.4655	0.6689	0.3269	0.0261	0.3969
0.6271	0.3676	0.0466	0.4178	0.6391	0.3552	0.0406	0.4385
0.5730	0.4176	0.0339	0.4979	0.6212	0.3719	0.0491	0.4450
0.5430	0.4454	0.0308	0.5263	0.6156	0.3777	0.0326	0.4571

and 443.15) K for the system with cumene and α-methylstyrene and between (383.15 and 493.15) K for the system with phenol. The detector was kept at 573.15 K to avoid water condensation.

Calibration was carried out taking known concentrations of each component, within the range of concentrations tested. Three to five volumes were withdrawn from each sample and injected into the columns. Relative deviations ± 1.0 % from the average value was obtained. While this method was adequate for most concentration ranges, it did not work well for the samples with low water concentration due to uncertainties related to the analytical balance measurements. A possible way to avoid this would be to sample a bigger volume, but this might disrupt the equilibrium of the system. The uncertainty on mass fraction measurement was range 0.0018 and 0.0051.

Results and Discussion

LLE Measurements. The experimental LLE results for (water + acetone + cumene), (water + acetone + phenol), and (water

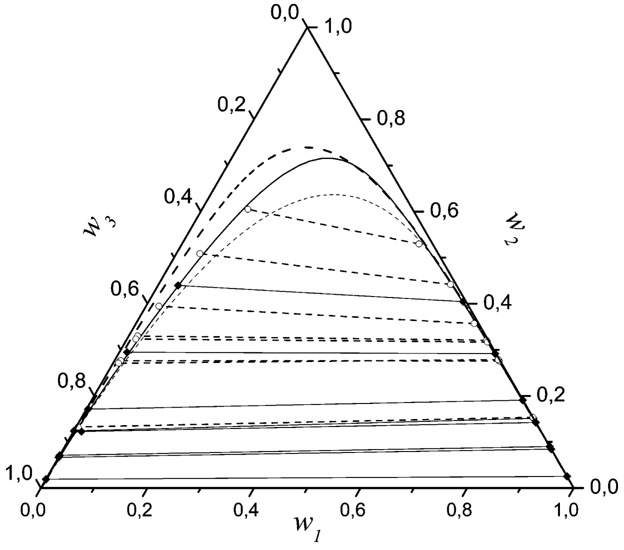

Figure 1. Liquid−liquid equilibria for the system water (1) + acetone (2) + cumene (3) at 323.15 K: ◆, this work; ○, Broglio;[1] ——, NRTL; - - -, UNIQUAC; — —, UNIFAC.

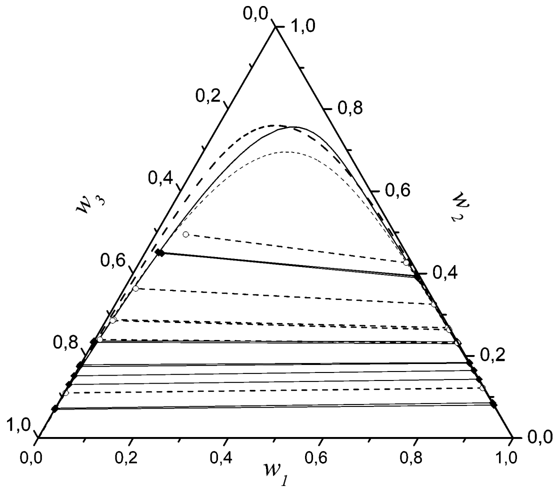

Figure 2. Liquid−liquid equilibria for the system water (1) + acetone (2) + cumene (3) at 333.15 K: ◆, this work; ○, Broglio;[1] ——, NRTL; - - -, UNIQUAC; — —, UNIFAC.

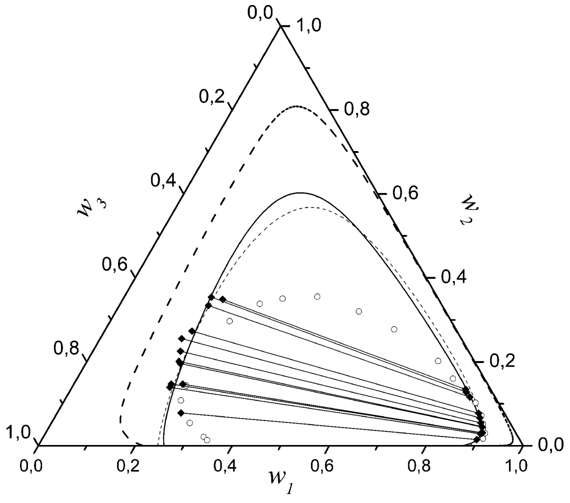

Figure 3. Liquid−liquid equilibria for the system water (1) + acetone (2) + phenol (3) at 323.15 K: ◆, this work; ○, Guttman and Wilczura [2]; ——, NRTL; - - -, UNIQUAC; — —, UNIFAC.

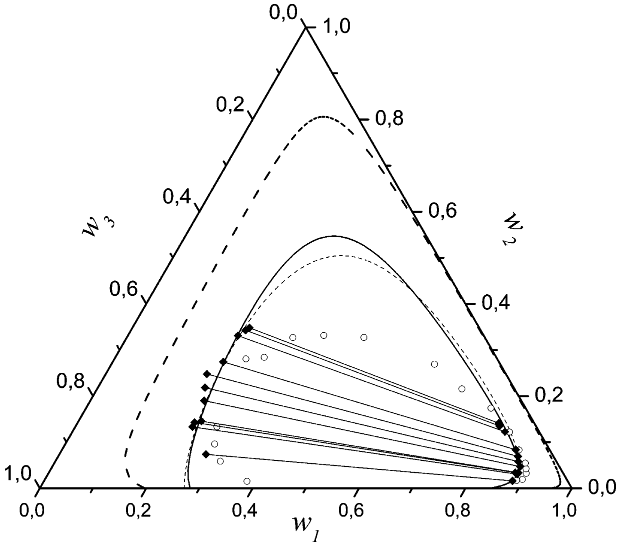

Figure 4. Liquid−liquid equilibria for the system water (1) + acetone (2) + phenol (3) at 333.15 K: ◆, this work; ○, Guttman and Wilczura;[2] ——, NRTL; - - -, UNIQUAC; — —, UNIFAC.

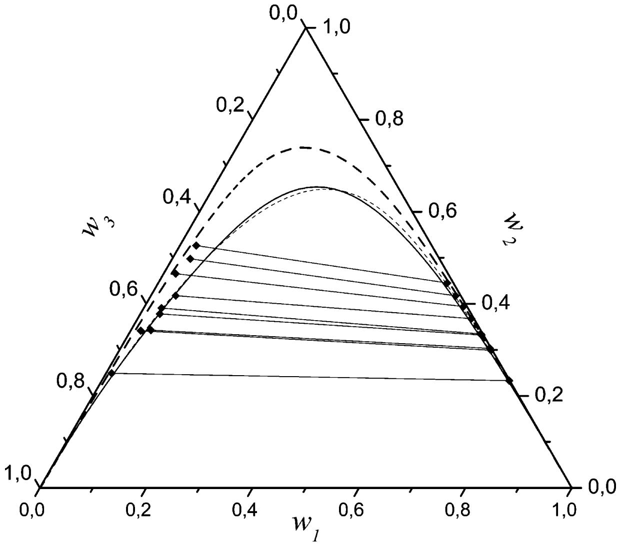

Figure 5. Liquid−liquid equilibria for the system water (1) + acetone (2) + ∝-methylstyrene (3) at 323.15 K: ◆, this work; ——, NRTL; - - -, UNIQUAC; — —, UNIFAC.

+ acetone + α-methylstyrene) systems are listed in Tables 1, 2, and 3 at temperatures of (323.15 and 333.15) K.

The results for (water + acetone + cumene) agree with thos from Broglio,[1] as shown in Figures 1 and 2. Figures 3 and 4 present the results for (water + acetone + phenol) as well as the results obtained by Guttman and Wilczura.[2] Agreement was good for low concentrations of acetone, but for high concentrations of acetone, it was not. The data obtained by Guttman and Wilczura[2] might have been strongly affected by the way the investigators obtained the concentrations: titration and visual detection of turning point. Another factor may have contributed for the differences: Guttman and Wilczura[2] worked with open cells while this work used sealed cells.

Figures 5 and 6 present the results for (water + acetone + α-methylstyrene). Extreme low quantity of water on the organic phase made it difficult to obtain data for this system, and some tie lines were discarded.

All systems investigated exhibited curves classified as type 1, as shown in Figures 1 to 6. It is clear, though, that the system water + acetone + phenol system tends to form diagrams of island type, which was mentioned by other investigators.[8,9] According to Novak et al.,[8] the island type behavior occurs in systems in which the associative effect is present. Prausnitz et al.[9] states that systems containing phenol tend to present associative effect, even at low concentrations, due to the hydroxyl group (-OH).

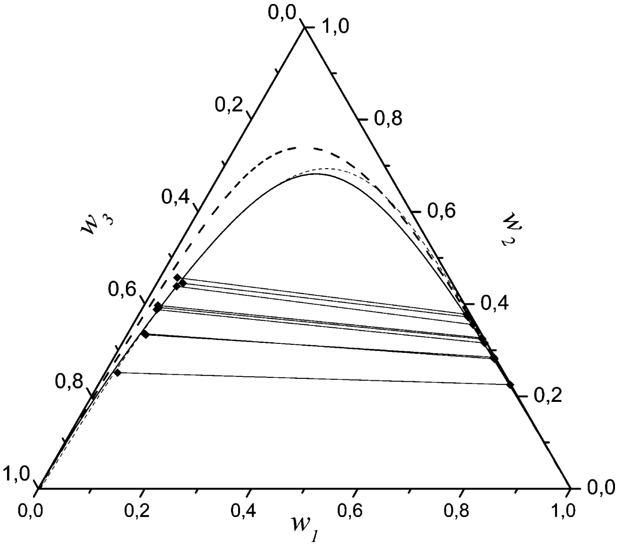

Figure 6. Liquid−liquid equilibria for the system water (1) + acetone (2) + ∝-methylstyrene (3) at 333.15 K: ◆, this work; ——, NRTL; - - -, UNIQUAC; — —, UNIFAC.

Table 4. UNIQUAC Model Parameters, *r* and *q*[7]

component	*r*	*q*
α-methylstyrene	5.0401	3.9560
acetone	2.5735	2.3360
cumene	5.0434	3.8160
phenol	3.5517	2.6800
water	0.9200	1.4000

Table 5. Fitted Parameters

	components	UNIQUAC		NRTL		
temp/K	*i*−*j*	A_{ij}/K	A_{ji}/K	A_{ij}/K	A_{ji}/K	α_{ij}
		Water (1) + Acetone (2) + Cumene (3)				
323.15	1−2	−199.57	−120.69	523.18	253.23	0.3411
	1−3	−403.53	3000.0	2818.8	1695.7	0.2655
	2−3	676.40	−691.31	556.87	−45.153	0.4700
333.15	1−2	−11.88	255.77	516.55	324.89	0.3411
	1−3	136.34	3000.0	2560.8	2213.9	0.2655
	2−3	59.88	151.39	604.08	−79.483	0.4700
		Water (1) + Acetone (2) + Phenol (3)				
323.15	1−2	−1044.4	3000.0	8.92	313.65	0.2000
	1−3	441.63	−221.47	1254.1	−101.14	0.3478
	2−3	319.33	−1357.9	−271.63	−1079.6	0.2895
333.15	1−2	−906.73	3000.0	128.21	257.78	0.2000
	1−3	437.63	−230.21	1259.8	−122.44	0.3478
	2−3	219.98	−1187.1	−308.40	−990.25	0.2895
		Water (1) + Acetone (2) + α-Methylstyrene (3)				
323.15	1−2	72.99	83.74	222.99	297.20	0.3311
	1−3	207.97	1238.3	3000.0	1885.4	0.2653
	2−3	−113.94	214.19	362.87	−388.87	0.4700
333.15	1−2	30.03	157.21	278.40	313.28	0.3311
	1−3	603.23	523.35	3000.0	1885.4	0.2653
	2−3	−115.89	219.63	390.93	−391.84	0.4700

Correlations. Values for the UNIQUAC model parameters, area (*r*) and volume (*q*), are presented in Table 4. These values as well as the ones that denote the interaction between the groups of the UNIFAC model follow the suggestions of Magnussen et al.[7] The NRTL[4] and UNIQUAC[5] models were used to correlate the experimental data. The parameters α_{ij}, related to the molecular nonrandom, and the interaction parameters A_{ij} were

Table 6. Global Standard Deviations

temp/K	NRTL	UNIQUAC	UNIFAC
Water (1) + Acetone (2) + Cumene (3)			
323.15	0.0028	0.0036	0.0151
333.15	0.0026	0.0028	0.0183
Water (1) + Acetone (2) + Phenol (3)			
323.15	0.0081	0.0080	0.0643
333.15	0.0079	0.0079	0.0788
Water (1) + Acetone (2) + α-Methylstyrene (3)			
323.15	0.0059	0.0035	0.0240
333.15	0.0052	0.0042	0.0225

treated as one single parameter during the fitting process. The FORTRAN program used to fit the models to the experimental results employed the nonlinear regression method based on the principle of maximum likelihood. The objective function (OF) to be minimized considered all measured properties and respective residues, as shown by eq 1, in which d is the number of data, N_k is the number of experimental data in each set, C_k is the number of components in each group, and δ is the standard deviation of each measured variable: temperature (T), composition of phase I (w^{I}), and composition of phase II (w^{II}):

$$\mathrm{OF} = \sum_{k=1}^{d} \sum_{j=1}^{N_k} \left\{ \left(\frac{T_{jk}^{\mathrm{cal}} - T_{jk}^{\mathrm{exp}}}{\delta T_{jk}} \right)^2 + \sum_{i=1}^{C_k - 1} \left[\left(\frac{w_{ijk}^{\mathrm{I,cal}} - w_{ijk}^{\mathrm{I,exp}}}{\delta w_{ijk}^{\mathrm{I}}} \right)^2 + \left(\frac{w_{ijk}^{\mathrm{II,cal}} - w_{ijk}^{\mathrm{II,exp}}}{\delta w_{ijk}^{\mathrm{II}}} \right)^2 \right] \right\} \quad (1)$$

The standard deviation for temperature was 0.15 K, while for the compositions were in the range [0.001 to 0.0023]. The fitted parameters are listed in Table 5. The low average values for the standard deviation and the good agreement between calculated and experimental results suggest that the models used are adequate to describe the experiments. Figures 1 to 6 show the high quality of the fitted models NRTL and UNIQUAC.

The UNIFAC model also described well the experimental results, except the system (water + acetone + phenol), in which the agreement was only qualitative (Figures 3 and 4). The larger difference, present in the system water + acetone + phenol is believed to be caused by the associative effect of this system.

Table 6 shows the average global standard deviations for each fitting performed by eq 2, in which i represents each component, j stands for each phase, and k represents each tie line:

$$\mathrm{rmsd} = \left(\sum_{k}^{n} \left[\frac{\sum_{i}^{3} \sum_{j}^{2} (w_{ijk,\mathrm{exp}} - w_{ijk,\mathrm{cal}})}{6n} \right] \right)^{1/2} \quad (2)$$

Conclusions

Experimental results were obtained for the LLE of the systems (water + acetone) with cumene or α-methylstyrene or phenol at temperatures of (323.15 and 333.15) K. Results were adequately described by the NRTL and UNIQUAC models for all systems and concentrations, except for the case with high acetone concentration in which results were strongly affected by its vapor pressure. All systems results were satisfactorily described by the UNIFAC model, except the water + acetone + phenol systems, in which the associative effect plays an important role.

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