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Ternary and Quaternary Liquid + Liquid Equilibria for Systems of (Water + Toluene + *m*-Xylene + Phenol)

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Tie line data for ternary systems containing phenol (C_6H_6O), water (H_2O), toluene (C_7H_8), and *m*-xylene (C_8H_{10}) were investigated. Phase diagrams of ternary systems of $\{w_1\ C_7H_8 + w_2\ C_6H_6O + (1 - w_1 - w_2)\ H_2O\}$ and $\{w_1\ C_8H_{10} + w_2\ C_6H_6O + (1 - w_1 - w_2)\ H_2O\}$ at 298.15 and 303.15 K were reported. The quaternary system $\{w_1\ C_8H_{10} + w_2\ C_7H_8 + w_3\ C_6H_6O + (1 - w_1 - w_2 - w_3)\ H_2O\}$ was also studied at 303.15 K. The experimental liquid−liquid equilibrium data have been correlated using the UNIQUAC and NRTL activity coefficient models, and the binary interaction parameters of these components have been presented. The correlated tie line results have been compared with the experimental data. The comparisons indicate the superiority of the NRTL activity coefficient model to UNIQUAC for liquid−liquid equilibrium correlation of studied systems. The tie line data of the studied systems also were correlated using the Hand method.

Introduction

Although phenol is a highly toxic chemical substance it is a valuable raw material in the production of various chemicals. Because the economical and environmental reasons phenol could be reclaimed from drinking and wastewaters. The maximum amount sanctioned by the world health organization in drinking waters is 0.001 $mg\cdot L^{-1}$.[1] The environmental legislation, concerning the harmless level of 0.5 ppm for phenol, makes it more difficult to find chemical separation processes able to achieve this restriction.[2] Because of the known limitations of the direct separation processes such as distillation for practical extraction of the constituent components of the nonideal mixtures, the indirect separation processes such as solvent extraction may be considered. Solvent extraction is a common separation process in various chemical, petrochemical, and oil industries. Many authors used single or mixed solvents to separate organic compounds from water; some of them studied the salt effect in this separation.[3,4] Experimental data for liquid−liquid equilibria (LLE) of systems including phenol and water are limited;[1,5] however, there are strategies for recovering phenol from wastewater.[2]

In this work, we report the LLE results for ternary systems of {toluene (1) + phenol (2) + water (3)} and {*m*-xylene (1) + phenol (2) + water (3)} at (298.15 and 303.15) K and the quaternary system of {*m*-xylene (1) + toluene (2) + phenol (3) + water (4)} at 303.15 K. The LLE data were correlated using the nonrandom two-liquid (NRTL)[6] and the universal quasi-chemical (UNIQUAC)[7] activity coefficient models to obtain the binary interaction parameters of these components. The experimental and correlated results are compared. According to these comparisons, the NRTL activity coefficient model is more applicable for LLE calculations for the studied mixtures.

Experimental Section

Chemicals. All materials including phenol, toluene, *m*-xylene, and *N*,*N*-dimethylformamide (DMF) were supplied by Merck Co. Inc., Germany. The purity of each of the components was checked by gas chromatography, and the results confirmed that the mass fraction purity was higher than 0.99. All compounds were used without further purification and were stored in a desiccator with a drying agent before use.

***Apparatus and Procedure*.** The experimental LLE data were determined by using a glass cell with a water jacket to maintain a constant temperature (± 0.1 K). The solutions were measured by mass using a Sartorius analytical balance (model A200S, accurate to 0.0001 g). The mixtures were prepared inside the cell and vigorously agitated with a magnetic stirrer. After several experiments and taking samples at different time intervals, it was found that increasing the agitation time (minimum time 2 h) and rest time (minimum time 10 h) had no considerable effect on equilibrium phase compositions. Therefore, the mixture was stirred vigorously for at least 2 h and then left to settle for at least 10 h. Then the mixture was split into two liquid phases, which become clear and transparent at equilibrium, with a well-defined interface. The samples of both phases were collected and analyzed. The gas−liquid chromatography (GLC) measurement with internal standard calibration was used to determine the composition of mixtures. The internal standard component must be chosen so that it is well-resolved from other peaks in the chromatogram. In this case, DMF was used as the internal standard. The operating condition of GLC measurements is given in Table 1. The mass fraction of water in the mixture was calculated via the following equation:

$$w_{H_2O} = (m - \textstyle\sum_i m_i)/m \qquad (1)$$

where m is the mass of the mixture and m_i is the mass of each hydrocarbon component in the mixture except water, which was obtained by GLC measurements. For the same mixtures, the mass fractions of water were also measured directly by Karl Fischer titration using a Metrohm device (KF Coulometer, 684, Switzerland), and the results were in agreement with the calculated values from eq 1 within ± 0.001. The total mass balance indicated that the composition of organic and water phases agree with the composition of the overall system.

The analysis was repeated at least two times. The average of these readings was taken for the component compositions. The

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Table 1. Operating Condition for Gas Chromatography Instrument

column	3 % OV-17 Csorb WHP 100−200 mesh
detector type	FID
detector temperature	533.15 K
injector temperature	533.15 K
oven temperature	$327.15\ \text{K (isotime} = 4\ \text{min)} \xrightarrow{298.15\ \text{K}\cdot\text{min}^{-1}} 443.15\ \text{K}$
carrier gas	nitrogen
flow rate	16 mL·min^{-1}

Table 2. Experimental LLE Data for Ternary Mixtures {Solvent (1) + Phenol (2) + Water (3)}[a]

w_1^{O}	w_2^{O}	w_1^{W}	w_2^{W}	S	K
{Toluene (1) + Phenol (2) + Water (3)} at 298.15 K					
0.611	0.080	0.002	0.012	22.0	6.9
0.584	0.092	0.001	0.012	23.2	7.6
0.500	0.263	0.001	0.029	37.2	9.1
0.434	0.362	0.001	0.035	48.2	10.2
0.470	0.357	0.002	0.033	60.5	10.8
{Toluene (1) + Phenol (2) + Water (3)} at 303.15 K					
0.573	0.009	0.001	0.001	15.9	6.6
0.571	0.112	0.001	0.012	28.9	9.3
0.532	0.206	0.002	0.016	46.7	12.5
0.477	0.295	0.001	0.022	56.1	13.1
0.411	0.367	0.007	0.023	68.6	15.7
{*m*-Xylene (1) + Phenol (2) + Water (3)} at 298.15 K					
0.830	0.017	0.000	0.010	10.3	1.6
0.743	0.084	0.000	0.021	22.2	3.9
0.724	0.200	0.000	0.028	90.1	7.1
0.672	0.254	0.001	0.029	116.6	8.8
0.524	0.453	0.000	0.034	560.0	13.4
{*m*-Xylene (1) + Phenol (2) + Water (3)} at 303.15 K					
0.779	0.049	0.000	0.007	39.4	6.8
0.689	0.189	0.000	0.025	61.2	7.6
0.607	0.323	0.000	0.031	143.9	10.4
0.499	0.441	0.000	0.035	200.0	12.5
0.500	0.451	0.002	0.036	247.0	12.7

[a] O is the organic-rich phase, and W is the water-rich phase.

Table 3. Experimental LLE Data for Quaternary Mixture {*m*-Xylene (1) + Toluene (2) + Phenol (3) + Water (4)}

w_1^{O}	w_2^{O}	w_3^{O}	w_1^{W}	w_2^{W}	w_3^{W}	S	K
{*m*-Xylene (1) + Toluene (2) + Phenol (3) + Water (4)} at 303.15 K							
0.470	0.428	0.049	0.000	0.004	0.018	51.4	2.7
0.418	0.400	0.150	0.000	0.004	0.026	162.2	5.6
0.363	0.398	0.201	0.000	0.005	0.030	170.6	6.7
0.404	0.328	0.338	0.000	0.005	0.034	225.2	7.0
0.277	0.317	0.381	0.002	0.006	0.055	282.6	7.5

Table 4. UNIQUAC Structural Parameters

component	r	q
toluene	3.9228	2.968
m-xylene	4.6570	3.536
phenol	3.5517	2.680
water	0.9200	1.400

Table 5. Estimated UNIQUAC Parameters for the Systems: a {w_1 C_7H_8 + w_2 C_6H_6O + (1 − w_1 − w_2) H_2O}; b {w_1 C_8H_{10} + w_2 C_6H_6O + (1 − w_1 − w_2) H_2O}; and c {w_1 C_8H_{10} + w_2 C_7H_8 + w_3 C_6H_6O + (1 − w_1 − w_2 − w_3) H_2O}

system	i	j	A_{ij}/kJ·mol^{-1}	A_{ji}/kJ·mol^{-1}
a	1	2	−1.255	0.628
	1	3	418.4	−1.883
	2	3	4.411	2.316
b	1	2	4.990	−2.092
	1	3	16.736	−1.674
	2	3	4.411	6.276
c	1	2	−2.510	−2.092
	1	3	−3.347	1.620
	1	4	8.368	137.507
	2	3	4.974	3.182
	2	4	7.634	12.552
	3	4	3.766	−2.316

Table 6. Estimated NRTL Parameters for the Systems: a {w_1 C_7H_8 + w_2 C_6H_6O + (1 − w_1 − w_2) H_2O}; b {w_1 C_8H_{10} + w_2 C_6H_6O + (1 − w_1 − w_2) H_2O}; and c {w_1 C_8H_{10} + w_2 C_7H_8 + w_3 C_6H_6O + (1 − w_1 − w_2 − w_3) H_2O}

system	i	j	A_{ij}/kJ·mol^{-1}	A_{ji}/kJ·mol^{-1}
a	1	2	−1.255	2.510
	1	3	23.012	−6.276
	2	3	9.205	7.702
b	1	2	10.277	−7.141
	1	3	18.828	−3.766
	2	3	6.276	7.702
c	1	2	2.564	−2.188
	1	3	−0.269	5.021
	1	4	18.828	−4.184
	2	3	10.241	7.113
	2	4	20.068	12.552
	3	4	10.137	6.276

reproducibility of the measured concentration of LLE was smaller than 0.2%, and the uncertainty for each mass fraction (w) and constant temperature (T) should be less than 0.001 and 0.1 K, respectively.

Results and Discussion

The measured mass fractions w of the equilibrium phases for systems of {toluene (1) + phenol (2) + water (3)} and {*m*-xylene (1) + phenol (2) + water (3)} at (298.15 and 303.15) K are presented in Table 2. Table 3 shows the measured mass fractions of the equilibrium phases for quaternary system of {*m*-xylene (1) + toluene (2) + phenol (3) + water (4)} at 303.15 K. For the studied ternary systems, the selectivity (S), as a measure of the ability of toluene (1) or *m*-xylene (1) to separate phenol (2) from water (3) is given by[8]

$$S = \frac{(w_2/w_3)^{O}}{(w_2/w_3)^{W}} \tag{2}$$

where the superscripts O and W indicate the organic-rich phase and the water-rich phase, respectively. This quantity is an important factor to examine the efficiency of solvent extraction processes.

The dissolving ability as a measure of the toluene or *m*-xylene required for the desired recovery of phenol is defined in the following form:[8]

$$K = \frac{w_2^{O}}{w_2^{W}} \tag{3}$$

The experimental values of S and K for the ternary systems were also presented in Table 2. For the quaternary systems, the mixture of *m*-xylene (1) and toluene (2) are considered as a mixed solvent. Therefore, the measured S and K as presented in Table 3 refer to efficiency evaluation of the mixed solvent for extraction of phenol from water.

The experimental tie line data were correlated using the UNIQUAC and NRTL activity coefficient models. For the UNIQUAC correlation, the pure component structural parameters (r and q) were calculated by the method outlined[7,9] and are listed in Table 4. The binary interaction parameters of the UNIQUAC and NRTL models for the studied systems are presented in Tables 5 and 6, respectively. All nonrandomness factors (α_{ij}) in the NRTL model were fixed and not adjusted during the correlation. Best results were obtained when α_{ij} were

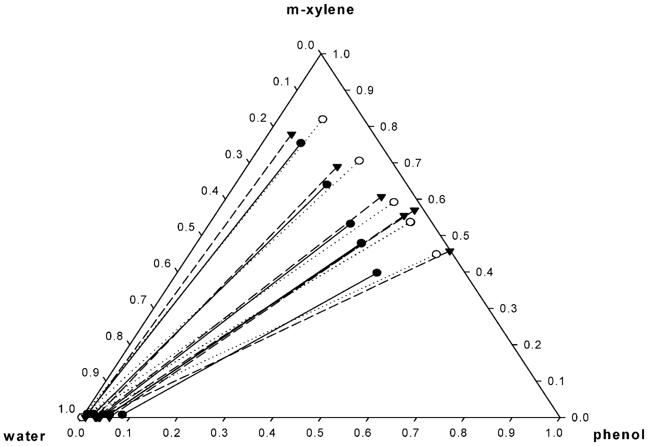

Figure 1. LLE data for system {*m*-xylene (1) + phenol (2) + water (3)} at 303.15 K: solid right-facing triangle, experimental tie line data; ●, NRTL model; ○, UNIQUAC model.

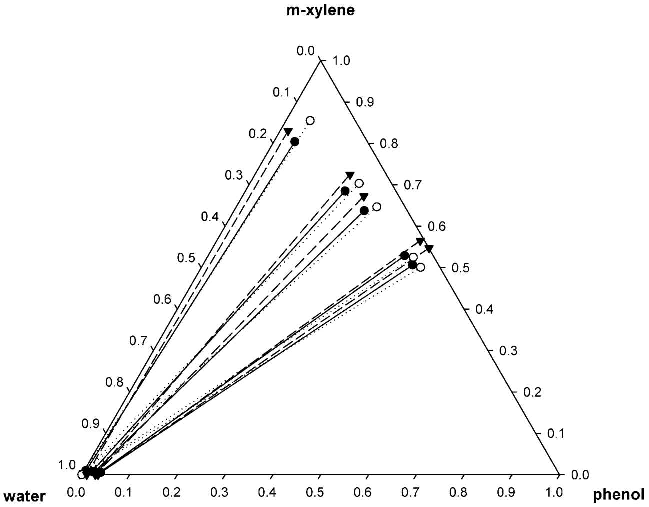

Figure 2. LLE data for system {*m*-xylene (1) + phenol (2) + water (3)} at 298.15 K: solid right-facing triangle, experimental tie line data; ●, NRTL model; ○, UNIQUAC model.

set at values of 0.20 for all used pairs. The phase diagrams for the studied ternary systems are presented in Figures 1 to 4.

The experimental data were correlated by using the UNIQUAC and NRTL models by minimizing the following objective function (OF):[8]

$$\mathrm{OF} = \sum_i \sum_j \sum_k (w_{ijk}^{\mathrm{exp}} - w_{ijk}^{\mathrm{cal}})^2 \tag{4}$$

where w^{exp} and w^{cal} are the experimental and calculated mass fractions, respectively, and the subscripts *i*, *j*, and *k* respectively designate the component, the phase, and the tie line. The root mean square deviation (rmsd) is a measure of the agreement between the experimental data and the calculated values. The rmsd value is defined as follows:[10]

$$\mathrm{rmsd} = [\sum_{i=1}^{n} \sum_{j=1}^{2} \sum_{k=1}^{M} (w_{ijk}^{\mathrm{exp}} - w_{ijk}^{\mathrm{cal}})^2/2nM]^{1/2} \tag{5}$$

where w_{ijk}^{cal} is the calculated mass fraction, $w_{ijk}^{\mathrm{exp}}$is the experimental ones, *i* is the number of components, *j* is the number of phases, *k* is the number of tie lines, and *M* is the total number of tie lines. The rmsd values are also listed in Table 7. The calculations based on both the UNIQUAC and NRTL models indicate a good fit with those of the representation of the tie line data for these systems. The calculated standard deviation σ for fitting the experimental data with UNIQUAC and NRTL models for the studied ternary and quaternary systems are reported in Table 8. The standard deviation σ is presented by the following equation:

$$\sigma = \left[\sum_{i=1}^{N} \frac{(w_{\mathrm{exp}} - w_{\mathrm{cal}})^2}{N - q}\right] \tag{6}$$

where *N* and *q* are respectively the number of experimental data and the required parameters for fitting the experimental mass

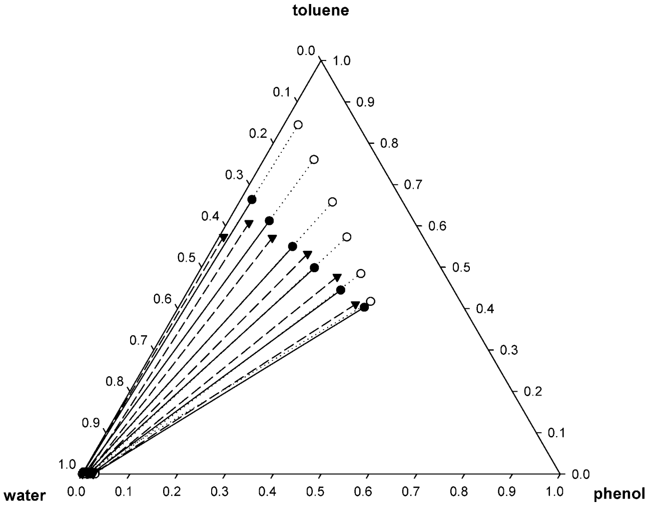

Figure 3. LLE data for system {toluene (1) + phenol (2) + water (3)} at 303.15 K: solid right-facing triangle, experimental tie line data; ●, NRTL model; ○, UNIQUAC model.

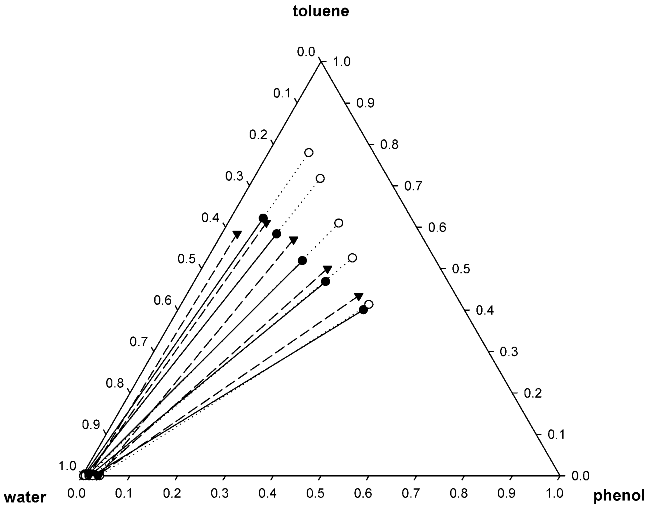

Figure 4. LLE data for system {toluene (1) + phenol (2) + water (3)} at 298.15 K: solid right-facing triangle, experimental tie line data; ●, NRTL model; ○, UNIQUAC model.

Table 7. Root Mean Square Deviation (rmsd) Values for the Studied Systems

	NRTL		UNIQUAC	
system	298.15 K	303.15 K	298.15 K	303.15 K
a	0.0288	0.0314	0.0785	0.0909
b	0.0245	0.0650	0.0319	0.0326
c		0.0177		0.0198

Table 8. Calculated Standard Deviation σ for the Studied Systems

	NRTL		UNIQUAC	
system	298.15 K	303.15 K	298.15 K	303.15 K
a	0.0032	0.0040	0.0216	0.0280
b	0.0020	0.0190	0.0030	0.0035
c		0.0012		0.0010

Table 9. Parameters of Equation 7 for the Systems: a {w_1 C_7H_8 + w_2 C_6H_6O + (1 − w_1 − w_2) H_2O}; b {w_1 C_8H_{10} + w_2 C_6H_6O + (1 − w_1 − w_2) H_2O}; and c {w_1 C_8H_{10} + w_2 C_7H_8 + w_3 C_6H_6O + (1 − w_1 − w_2 − w_3) H_2O}

system	T/K	*a*	*b*
a	298.15	0.0417	0.6283
	303.15	0.0332	0.8113
b	298.15	0.0412	0.3417
	303.15	0.0437	0.6129
c	303.15	0.0574	0.4158

fraction data with the applied models. The experimental data for the studied ternary systems were correlated by the following equation proposed by Hand:[11]

$$\frac{w_2^{\mathrm{W}}}{w_3^{\mathrm{W}}} = a\left[\frac{w_2^{\mathrm{O}}}{w_1^{\mathrm{O}}}\right]^b \qquad (7)$$

represents a linear dependency of the ratio $w_2^{\mathrm{O}}/w_3^{\mathrm{O}}$ on the ratio $w_2^{\mathrm{s}}/w_1^{\mathrm{s}}$ in logarithmic coordinates and for studied systems parameters *a* and *b* are listed in Table 9.

Conclusions

LLE data of the ternary systems {toluene (1) + phenol (2) + water (3)} and {*m*-xylene (1) + phenol (2) + water (3)} at (298.15 and 303.15) K and the quaternary system of {*m*-xylene (1) + toluene (2) + phenol (3) + water (4)} at 303.15 K are reported. The UNIQUAC and NRTL activity coefficient models satisfactorily correlated the LLE experimental data of the studied systems, and the parameters of these models are presented. Both models accurately correlate the experimental tie line data, although the NRTL model is slightly better except for the system of {*m*-xylene (1) + phenol (2) + water (3)} at 303.15 K. The obtained results indicate that, for the quaternary system, both models correlate LLE data with good accuracy. The calculated overall rmsd for equilibrium phases mass fractions are less than 0.065 and 0.091 for NRTL and UNIQUAC models, respectively.

The aim of this work was to investigate the role the single solvent (*m*-xylene or toluene) and mixed solvent (*m*-xylene + toluene) in extracting phenol from (phenol + water) mixtures in order to compare and clarify the efficiency of the single solvent (*m*-xylene or toluene) and mixed solvents (*m*-xylene + toluene) in the extraction of phenol from (phenol + water) mixtures.

From the selectivity values, the separation of phenol from water by extraction with aromatic compounds such as toluene and m-xylene is feasible. The obtained selectivity results for the systems {toluene (1) + phenol (2) + water (3)} and {*m*-xylene (1) + phenol (2) + water (3)} show that, for systems containing *m*-xylene, selectivity is higher. Therefore, by considering the technical and economical viewpoints in a practical extraction, the *m*-xylene solvent and mixed solvent (*m*-xylene + toluene) operations may be preferred. The obtained experimental selectivity (*S*) and the dissolving ability (*K*) indicated that the efficiency of extraction of phenol from water by *m*-xylene or toluene at 303.15 K is higher than 298.15 K.

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