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Liquid−Liquid(−Liquid) Equilibria in Ternary Systems of Aliphatic Hydrocarbons (Heptane or Octane) + Phenols + Water

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S *Supporting Information*

ABSTRACT: The liquid−liquid equilibria (LLE) and liquid−liquid−liquid equilibria (LLLE) in eight ternary systems were determined by photometric turbidity titration at atmospheric pressure. Additionally, the compositions of coexisting phases were determined with analytic methods. The measurements in the systems heptane or octane + phenol + water were realized at temperatures of (313.15 and 333.15) K. The equilibrium data in the systems heptane + 2-cresol or 3-cresol or 4-cresol + water and octane + 2-cresol or 3-cresol or 4-cresol + water were estimated at temperatures of (298.15 and 323.15) K. The excess Gibbs energy nonrandom two-liquid (NRTL) and universal quasichemical (UNIQUAC) activity coefficient models as well as the Elliott−Suresh−Donohue equation of state (ESD EoS) were used to predict the LLE or LLLE in the investigated ternary systems. The binary interaction parameters were calculated using vapor−liquid and LLE data from the literature or data predicted with the modified universal quasichemical functional-group activity coefficient (UNIFAC Dortmund) model.

INTRODUCTION

An optimized planning and realization of extraction plants in chemical industry require comprehensive qualitative and quantitative phase equilibrium data. Aside from an accurate equipment configuration, the experimental data are essential for the judgment of different prediction methods. In this publication the prediction results of the models nonrandom two-liquid (NRTL)[1] and universal quasichemical (UNIQUAC)[2] and the Elliott−Suresh−Donohue equation of state (ESD EoS)[3,4] are compared with the experimental liquid−liquid equilibrium (LLE) and liquid−liquid−liquid equilibrium (LLLE) data of the investigated ternary systems. Aliphatic hydrocarbons are components that are used as solvent or as extraction or cleaning agent in the chemical industry and as well as fuel additive to improve the knock resistance behavior of fuels. Phenols are components of coal tar and are used as a disinfectant and a preservative, taking advantage of their bactericidal and fungicidal performance. The technical importance of the selected substance combinations emerges for instance in the regeneration of polluted groundwater in former industrial locations or the ground contaminations of historical coking plants.

EXPERIMENTAL SECTION

Materials. The components 2-cresol, 3-cresol, 4-cresol, and octane were purchased from Merck-Schuchardt (Hohenbrunn, Germany), as well as heptane from Acros Organics, Belgium, with purities of > 99 % in mass. Phenol was obtained from Berlin Chemie (Berlin, Germany), with a purity of > 98 % in mass, and Merck-Schuchardt (Hohenbrunn, Germany), with a purity of > 99.5 % in mass. The components were distilled twice in a Vigreux column at reduced pressure under a N_2 atmosphere or in a bubble tray column at normal pressure. The mass fraction verification of all investigated components by gas−liquid chromatography (GLC) resulted as follows: phenol (> 99.7 %), 2-cresol (> 99.1 %), 3-cresol (> 99.8 %), 4-cresol (> 99.8 %), heptane (> 99.6 %), and octane (> 99.5 %). The pure component density measurements were realized with a vibrating tube density meter (DMA 58, Anton Paar, Austria), and they are in agreement with the published data as listed in the Supporting Information. Deionized and distilled water was used in all experiments.

Methods. The determination of the binodal curves were realized by photometric turbidity titration. Reliable binodal curve measurements in different ternary systems have been obtained with this method, for example, water + cyclohexylamine + aromatic or aliphatic hydrocarbons published by Klauck et al.[5] The experimental setup includes a temperature-controlled glass vessel with a magnetic stirrer, an ultrasonic generator (UW 2070, Bandelin Electronic, Berlin), a photometer (type 622, Deutsche Metrohm, Filderstadt), and an automatic buret (716 DMS Titrino, Deutsche Metrohm, Filderstadt). For the experimental determination of equilibrium data one of the components for binary systems or a binary homogeneous mixture is prepared in the vessel. With an automatic buret the second or third component is added in small amounts of 0.02 mL into the vessel and dispensed via a low power ultrasonic generator. The photometer light transmission measurement indicates the solubility limit due to an intensive turbidity, whereas the data is logged with a personal computer. The equilibrium compositions of the liquid phases in binary and ternary systems are determined with an uncertainty of $\pm$ 0.003 $\text{mol} \cdot \text{mol}^{-1}$ and a temperature uncertainty of $\pm$ 0.1 K.

The determination of the coexisting phases is carried out by means of analytic methods. Through the application of a temperature-regulated glass vessel with sampling points at

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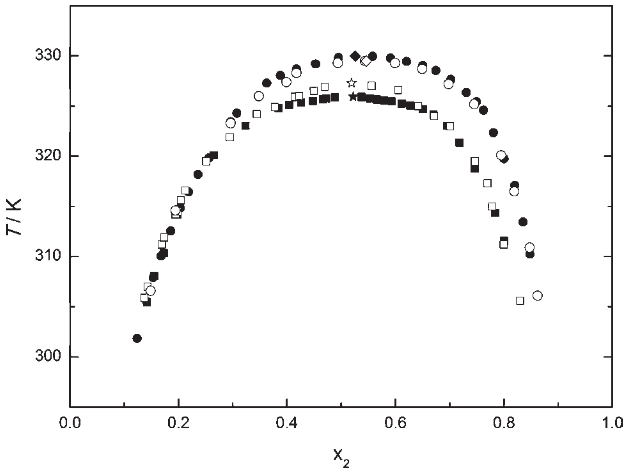

Figure 1. Experimental LLE in the systems: ■, heptane (1) + phenol (2) with ★, the upper critical solution point; ●, octane (1) + phenol (2) with ◆, the upper critical solution point (this work); □, heptane (1) + phenol (2) with ☆, the upper critical solution point; ○, octane (1) + phenol (2) with ◇, the upper critical solution point (ref 7).

Table 1. Pure Component Parameters for the ESD EoS

substance	ref	c^a	ε_j/k^b K	b^c $cm^3 \cdot mol^{-1}$	$\varepsilon_{HB}/RT_{crit}{}^d$	$\kappa_{AB}/v^{*\,e}$
phenol	9	1.6503	415.407	34.391	3.0470	0.02936
2-cresol	9	1.1983	607.630	42.618	4.3269	0.00098
3-cresol	9	1.6317	444.525	41.836	3.3574	0.01201
4-cresol	9	2.0758	359.595	40.150	2.2174	0.1517
heptane	19	2.3002	280.690	47.761		
octane	19	2.2842	285.211	54.157		
water	19	1.0053	427.254	9.411	4.0000	0.1000

[a] Shape factor for the repulsive term. [b] Potential energy well depth of dispersion term. [c] Volume parameter. [d] Potential energy well depth of hydrogen bond. [e] Measure of bonding volume.

different heights, it is possible to get a separate sample of each phase. Defined mixtures of the components are prepared in the vessel, and the phases are equilibrated by intensive stirring. A complete phase separation is guaranteed by a waiting period for at least 24 h at constant temperature with an uncertainty of ± 0.1 K. Afterward, samples of each phase are taken and prepared for the following analysis. The composition of both organic phases is analyzed by a GLC method. A Hewlett-Packard 6890 series gas chromatograph with a flame ionization detector and an HP Ultra 2 column (cross-linked poly(5 %-phenyl methyl)siloxane) is used. The analysis of the composition is based on the method of an internal standard. The organic components are determined with an uncertainty of ± 0.005 $mol \cdot mol^{-1}$ by the GLC analysis. The content of water is calculated by subtraction from unity.

The composition of the water-rich phase is determined by titration methods. The phenol content is measured by quantitative conversion with bromine.[6] The uncertainty for the organic component phenol with potentiometric titration via an automatic buret (716 DMS Titrino, Deutsche Metrohm, Filderstadt) and a platinum-annular electrode is 1 % in mass of the measured value. The water content determined by Karl Fischer titration has an uncertainty of 1 % in mass of the measured value. The octane content is appraised by means of binary water solubility data; therefore, the compositions of the water-rich phase result in an uncertainty of ± 0.01 $mol \cdot mol^{-1}$.

■ RESULTS AND DISCUSSION

Experimental Data. The LLE in the binary systems of heptane or octane with phenol are determined over the whole temperature range at atmospheric pressure. The experimental data are reported in the Supporting Information. The LL(L)E in the eight ternary systems are measured at two different temperatures at atmospheric pressure. The occurrence of three-phase regions requires the application of the GLC method beside the photometric turbidity titration. The ternary experimental LLE and LLLE data are represented in the Supporting Information.

Both binary systems heptane and octane with phenol show a temperature-dependent miscibility gap. The upper critical solution point is reached at a lower temperature in the heptane + phenol

Table 2. Parameters and Deviations of Binary Systems for the ESD EoS (eq 3)

binary system	fitted data	k_{ij}^C	k_{ij}^T K^{-1}	k_{ij}^{TT} K^{-1}	ΔP^a %	Δy^b	Δx^b
heptane (1) + water (2)[c]		0.134979	0.00093568		5.20	0.0563	0.0003
heptane (1) + 2-cresol (2)	UNIFAC prediction	−0.043750	0.00051163		8.48	0.0030	
heptane (1) + 3-cresol (2)	UNIFAC prediction	−0.012030	0.00011834		3.51	0.0024	
heptane (1) + 4-cresol (2)	UNIFAC prediction	−0.003856	0.00001627		2.09	0.0053	
octane (1) + water (2)[c]		0.154728	0.00066375		5.97	0.0176	0.0003
octane (1) + phenol (2)	this work, 13	0.129129	0.00055143	−0.004111941	1.31	0.0073	0.0319
octane (1) + 2-cresol (2)[d]		0.041330	0.00056014		2.46	0.0066	
octane (1) + 3-cresol (2)[d]		−0.031437	0.00043516		2.67	0.0072	
octane (1) + 4-cresol (2)	15, 16	0.003589	0.00005497		4.18	0.0025	0.0034
water (1) + phenol (2)[d]		0.044292	0.00014692		5.25	0.0173	0.0280
water (1) + 2-cresol (2)[d]		0.036015	0.00045420		3.13	0.0009	0.0056
water (1) + 3-cresol (2)[d]		0.052246	0.00027514		1.81	0.0035	0.0101
water (1) + 4-cresol (2)[d]		0.045770	0.00017819		5.05	0.0073	0.0095

[a] $\Delta P = 100/n_p \cdot \Sigma(|P_{calcld} - P_{exptl}|/P_{exptl})$, where n_p is the number of data points. [b] $\Delta Z = 1/n_p \cdot \Sigma|Z_{calcld} - Z_{exptl}|$, where Z represents x or y. [c] Parameter taken from ref 5. [d] Parameter taken from ref 9.

Table 3. Parameters and Deviations of Binary Systems for the NRTL and UNIQUAC Models (eq 1)

			C_{12}^C	C_{21}^C			ΔP^a		
binary system	fitted data	model	K	K	C_{12}^T	C_{21}^T	%	Δy^b	Δx^b
heptane (1) + water (2)[c]		NRTL (α = 0.20)	2028.97	3497.63	−5.6490	10.4226	4.11	0.0276	0.000094
		UNIQUAC	1398.94	525.20	−4.1248	1.7004	4.16	0.0279	0.000099
heptane (1) + phenol (2)	this work, 12, 13	NRTL (α = 0.20)	434.53	274.41	−0.3136	1.5736	6.09	0.0105	0.102276
		UNIQUAC	289.94	−55.64	1.0700	−0.2126	3.37	0.0095	0.089037
heptane (1) + 2-cresol (2)	UNIFAC prediction	NRTL (α = 0.47)	649.48	213.09	−0.6767	0.3855	1.33	0.0005	
		UNIQUAC	349.79	−113.73	0.0299	−0.0754	0.01	0.0001	
heptane (1) + 3-cresol (2)	UNIFAC prediction	NRTL (α = 0.47)	605.24	223.56	−0.5748	0.3915	6.05	0.0003	
		UNIQUAC	349.79	−113.72	0.0299	−0.0755	4.46	0.0001	
heptane (1) + 4-cresol (2)	UNIFAC prediction	NRTL (α = 0.47)	605.20	223.60	−0.5742	0.3909	0.01	0.0001	
		UNIQUAC	319.94	−101.93	0.0992	−0.0855	1.26	0.0002	
octane (1) + water (2)[c]		NRTL (α = 0.20)	2141.80	3260.80	−7.5243	12.5591	2.67	0.0169	0.000040
		UNIQUAC	1558.09	381.79	−5.8408	1.8703	2.71	0.0168	0.000042
octane (1) + phenol (2)	this work, 13	NRTL (α = 0.25)	378.48	405.11	−0.2610	1.4775	2.30	0.0066	0.074821
		UNIQUAC	282.11	−42.67	0.5226	−0.1023	1.85	0.0073	0.077840
octane (1) + 2-cresol (2)[d]		NRTL (α = 0.51)	707.78	579.79	−2.8088	−1.4006	1.06	0.0019	
		UNIQUAC	286.41	−57.92	0.0066	−0.2871	1.35	0.0014	
octane (1) + 3-cresol (2)[d]		NRTL (α = 0.40)	606.70	−244.16	−1.2432	7.3141	2.31	0.0031	
		UNIQUAC	519.83	−266.85	−2.7093	2.3092	1.86	0.0027	
octane (1) + 4-cresol (2)	15, 16	NRTL (α = 0.47)	1295.72	250.58	−5.7218	1.2463	2.13	0.0091	
		UNIQUAC	602.87	−221.38	−1.8934	0.8309	2.62	0.0091	
water (1) + phenol (2)[d]		NRTL (α = 0.20)	1821.63	−557.19	−5.0783	1.5755	6.35	0.0185	0.0250
		UNIQUAC	467.34	−216.70	0.6408	−0.9202	5.03	0.0189	0.0116
water (1) + 2-cresol (2)[d]		NRTL (α = 0.40)	1470.53	439.33	1.8177	−3.1878	0.67	0.0017	0.0030
		UNIQUAC	569.14	−181.64	−1.4436	0.1756	0.86	0.0012	0.0411
water (1) + 3-cresol (2)		NRTL (α = 0.20)[e]	1397.66	−253.30	1.7107	−0.9899	4.62	0.0035	0.0174
		UNIQUAC[d]	41.34	74.19	−1.5048	1.7006	2.72	0.0033	0.0086
water (1) + 4-cresol (2)[d]		NRTL (α = 0.20)	1502.87	−307.39	4.4922	−1.8663	0.61	0.0110	0.0119
		UNIQUAC	243.42	−87.22	0.6966	−0.7445	0.98	0.0105	0.0068

[a] $\Delta P = 100/n_p \cdot \Sigma(|P_{\mathrm{calcld}} - P_{\mathrm{exptl}}|/P_{\mathrm{exptl}})$, where n_p is the number of data points. [b] $\Delta Z = 1/n_p \cdot \Sigma|Z_{\mathrm{calcld}} - Z_{\mathrm{exptl}}|$, where Z represents x or y. [c] Parameter taken from ref 5. [d] Parameter taken from ref 9. [e] Parameter taken from ref 18.

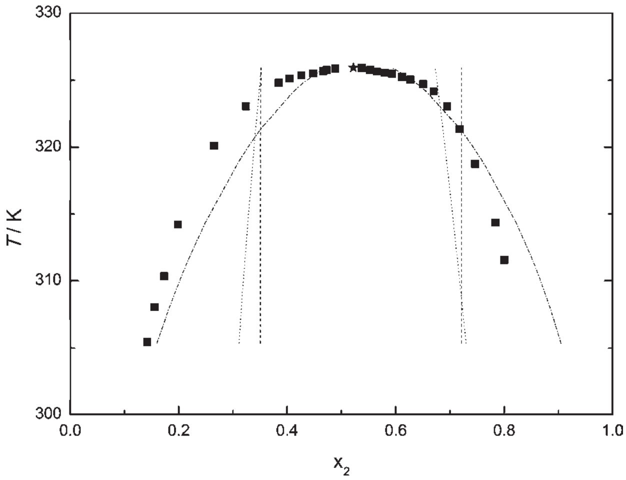

Figure 2. Results of calculation in the heptane (1) + phenol (2) system: ■, experimental data with ★, the upper critical solution point; dashed−dotted line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

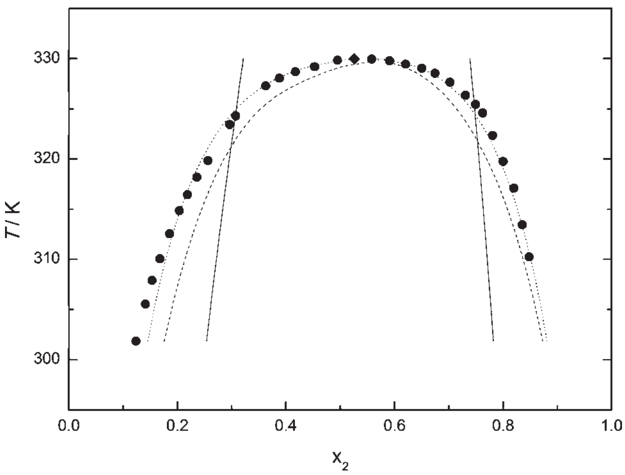

Figure 3. Results of calculation in the octane (1) + phenol (2) system: ●, experimental data with ◆, the upper critical solution point; NRTL model: solid line, four adjusted parameters; dashed line, five adjusted parameters; dotted line, six adjusted parameters.

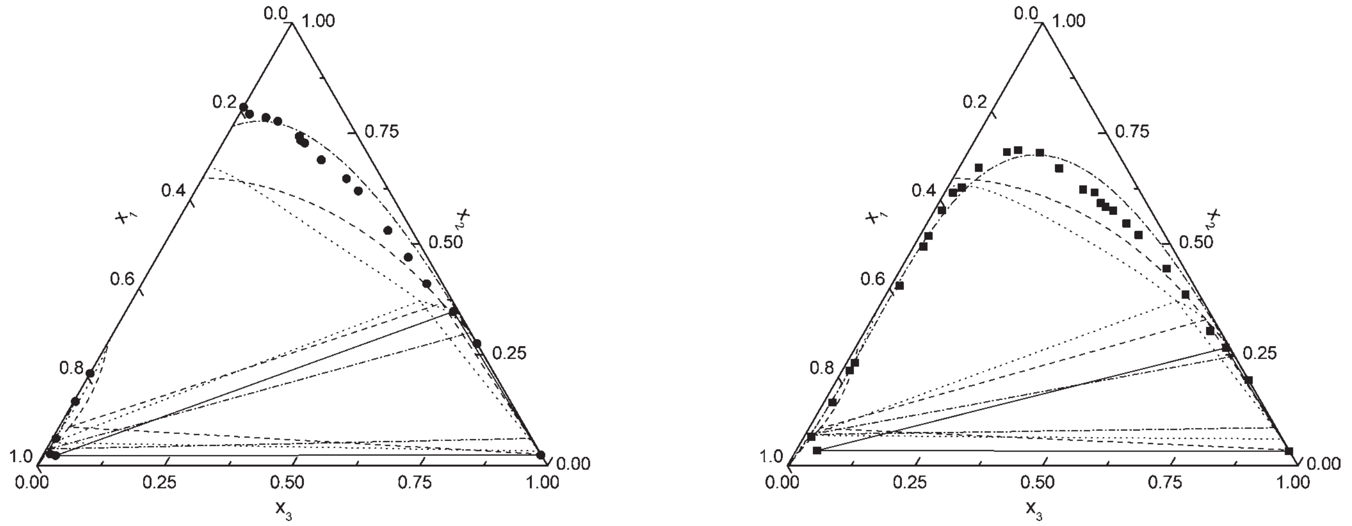

Figure 4. Results of prediction in the heptane (1) + phenol (2) + water (3) system. Experimental binodal curve and three-phase region: ●, solid line at 313.15 K; ■, solid line at 333.15 K. Predicted binodal curve and three-phase region: dashed−dotted line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

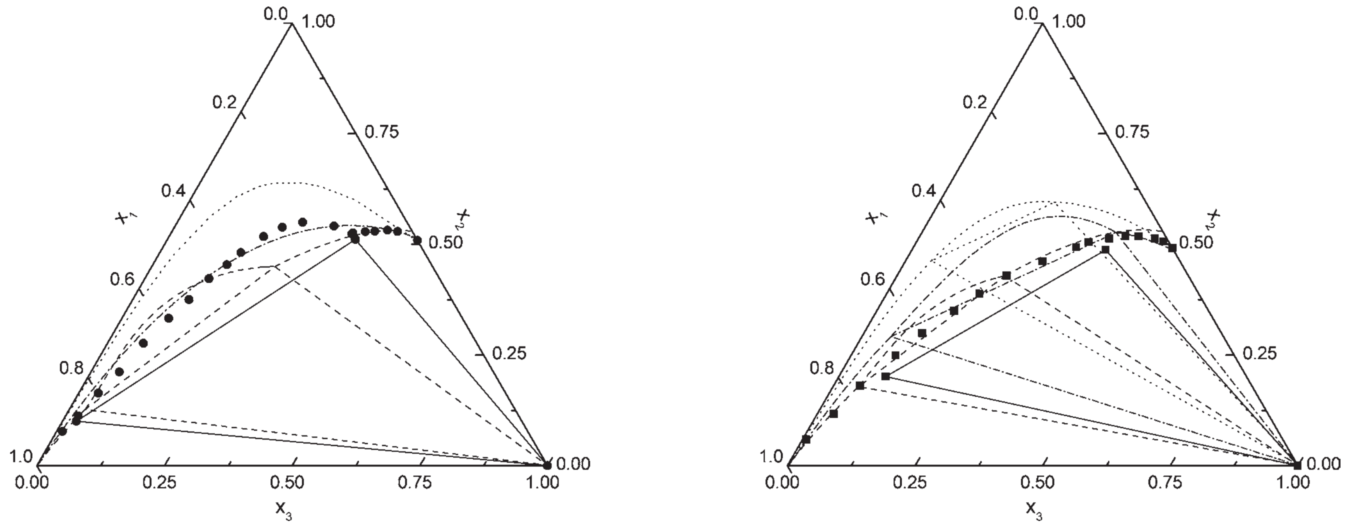

Figure 5. Results of prediction in the heptane (1) + 2-cresol (2) + water (3) system. Experimental binodal curve and three-phase region: ●, solid line at 298.15 K; ■, solid line at 323.15 K. Predicted binodal curve and three-phase region: dashed−dotted line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

system than in the octane + phenol system. The experimental data are summarized in Figure 1 compared with data published by Matsuda et al.[7]

In contrast, the binary mixtures of aliphatic hydrocarbons + 2-, 3-, or 4-cresol are homogeneous over the whole concentration and temperature range. A large miscibility gap occurs in the binary mixtures of hydrocarbons + water, which is correlated by Tsonopoulos.[8] The solubility of water in the phenols rises with increasing temperature; phenol shows the strongest temperature dependence followed by 4-cresol and 3-cresol and a significantly lower temperature dependence with 2-cresol. Only at 298.15 K is the solubility of water higher in 2-cresol than in 3-cresol. The experimental solubility data of water + 2-, 3-, and 4-cresol were published by Klauck et al.[9] and water + phenol by Martin et al.[10]

All investigated ternary systems show a comparable temperature behavior: the miscibility gap as well as the three-phase region decreases with increasing temperature. The experimental data and the prediction results are presented in Figures 4 through 11. The equilibrium properties are influenced primarily by the phenols. Both ternary systems with phenol are identified by a phase split in the binary systems heptane or octane + phenol at 313.15 K. The binary measurements show that the miscibility gap is closed at the second measuring temperature at 333.15 K. Compared to the cresol systems, the phenol systems are identified by the smallest three-phase region. The experimental data in the cresol systems are characterized by minor differences between the binodal curves as well as the size and position of the three-phase region. With increasing temperature the size of the three-phase region is decreasing in following order: 2-cresol, 3-cresol, and 4-cresol. The influence of the investigated aliphatic hydrocarbons heptane and octane is reflected by a smaller heterogeneous region for all ternary systems containing heptane

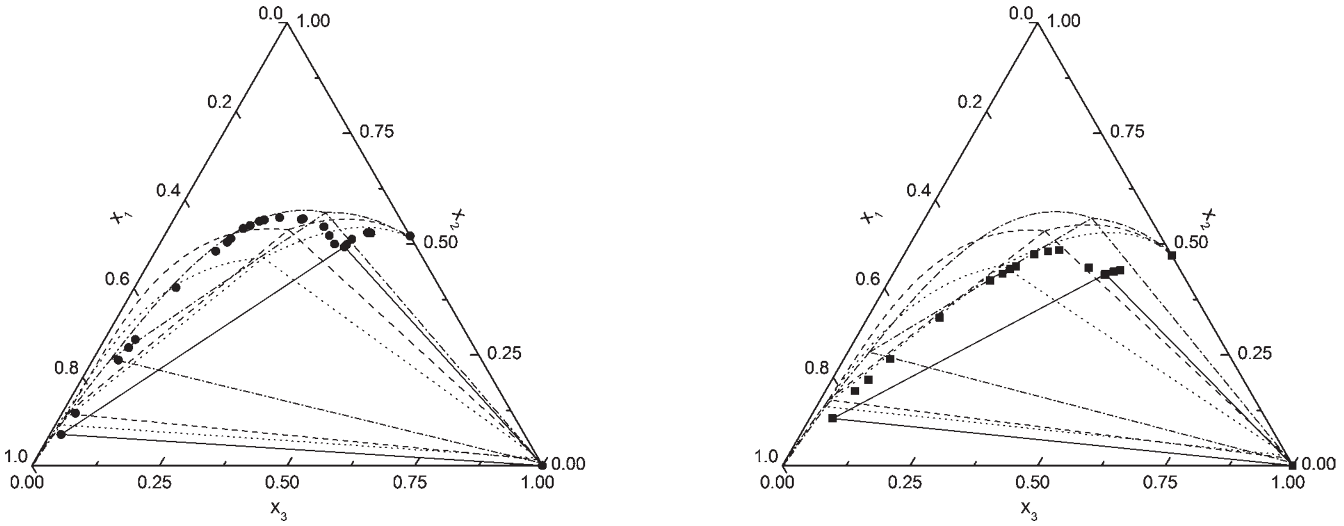

Figure 6. Results of prediction in the heptane (1) + 3-cresol (2) + water (3) system. Experimental binodal curve and three-phase region: ●, solid line at 298.15 K; ■, solid line at 323.15 K. Predicted binodal curve and three-phase region: dashed−dotted line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

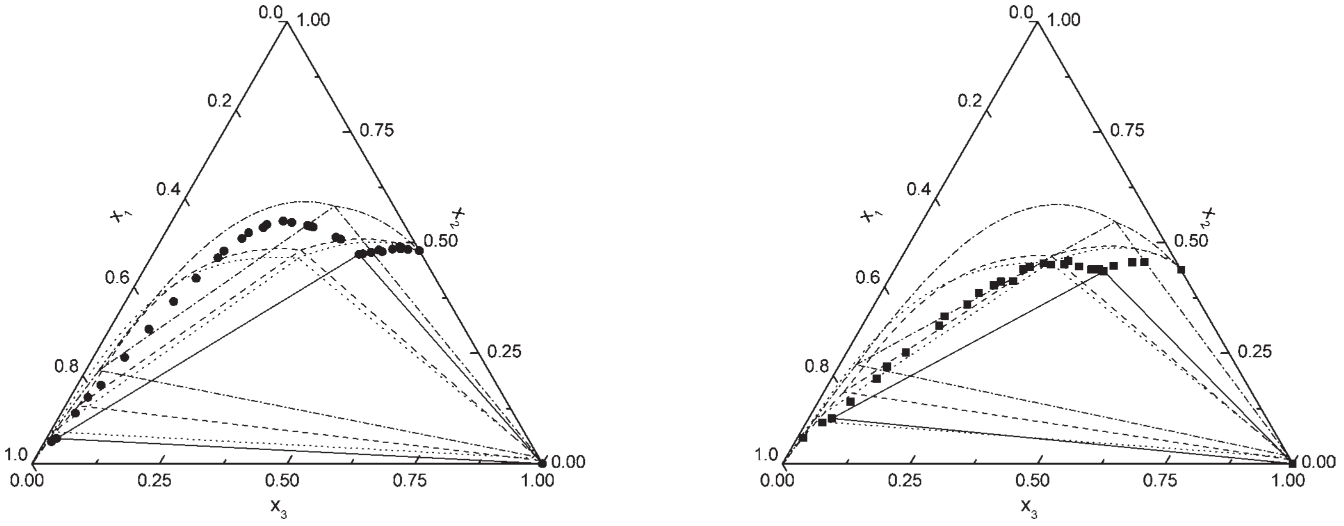

Figure 7. Results of prediction in the heptane (1) + 4-cresol (2) + water (3) system. Experimental binodal curve and three-phase region: ●, solid line at 298.15 K; ■, solid line at 323.15 K. Predicted binodal curve and three-phase region: dashed−dotted line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

at both investigated temperatures. Experimental investigations in the systems containing cresols show a water-rich phase consisting nearly of pure water; therefore, no experimental data was determined. Only for the system octane + phenol + water experimental data are determined in the water-rich phase at both temperatures. The ternary experimental data yielded in almost identical compositions of phenol and water compared to the binary solubility. The influence of the third component, octane, is minor and estimated by means of binary LLE data. Therefore, the same composition is used to plot the water-rich phase in the heptane + phenol + water system.

Correlations and Predictions. All available experimental data in the corresponding binary systems are correlated using the excess Gibbs energy models UNIQUAC and NRTL and the ESD EoS. Linear temperature-dependent binary interaction parameters are supposed for the activity coefficient models (eq 1)

$$C_{ij}/\mathrm{K} = C_{ij}^{C}/\mathrm{K} + C_{ij}^{T}(T/\mathrm{K} - 273.15) \qquad (1)$$

where $C_{ij} = (u_{ij} - u_{jj})/R$ for UNIQUAC and $C_{ij} = (g_{ij} - g_{jj})/R$ for NRTL. The objective function of Renon et al.[11] was used to estimate the parameters

$$Q = \Pi_1 \sum_i \left(\frac{100}{P_{\mathrm{exptl}}}\right)_i^2 (P_{\mathrm{calcld}} - P_{\mathrm{exptl}})_i^2 + \Pi_2 \sum_i (100)^2 \times (y_{1,\mathrm{calcld}} - y_{1,\mathrm{exptl}})_i^2 + \Pi_3 \sum_i (100)^2 (x'_{1,\mathrm{calcld}} - x'_{1,\mathrm{exptl}})_i^2 + \Pi_4 \sum_i (100)^2 (x''_{1,\mathrm{calcld}} - x''_{1,\mathrm{exptl}})_i^2 \qquad (2)$$

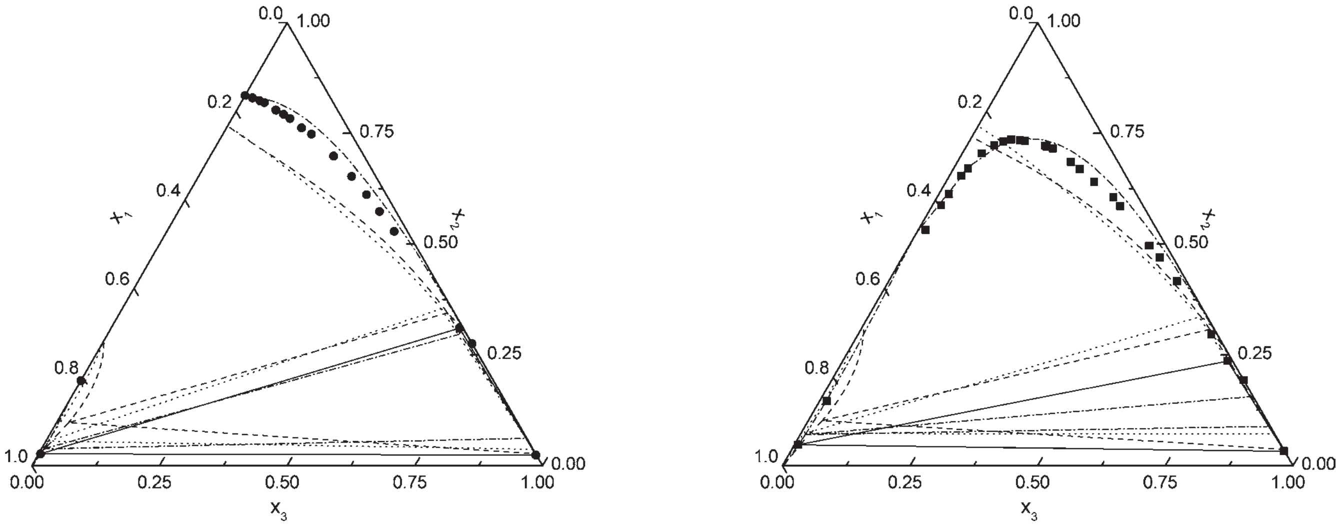

Figure 8. Results of prediction in the octane (1) + phenol (2) + water (3) system. Experimental binodal curve and three-phase region: ●, solid line at 313.15 K; ■, solid line at 333.15 K. Predicted binodal curve and three-phase region: dashed−dotted line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

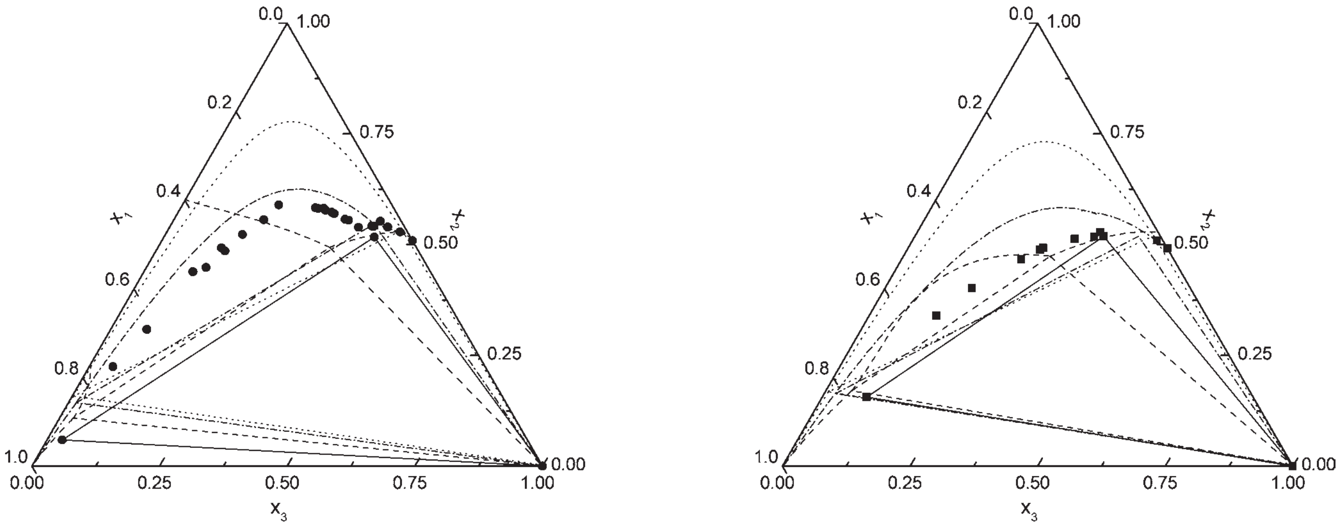

Figure 9. Results of prediction in the octane (1) + 2-cresol (2) + water (3) system. Experimental binodal curve and three-phase region: ●, solid line at 298.15 K; ■, solid line at 323.15 K. Predicted binodal curve and three-phase region: dashed−dotted line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

where P stands for pressure; y represents the vapor mole fraction; x' and x'' are the mole fractions of the different phases at LLE; and Π_i is a weighting factor. The fixing of the weighting factors depends on the available data. In principle, a small weighting factor is used for the vapor mole fraction; the weighting factors for pressure and mole fraction of the different liquid phases are adjusted to balance the different amounts of experimental data. The binary ESD EoS parameters k_{ij} are assumed to depend linearly on temperature (if $k_{ij}^{TT} = 0$) or to have an extended temperature function (eq 3):

$$k_{ij} = k_{ij}^{C} + k_{ij}^{T}/\mathrm{K}^{-1}(T/\mathrm{K} - 273.15) + k_{ij}^{TT}/\mathrm{K}^{-1} \times \left(T/\mathrm{K}\cdot\ln\left(\frac{298.15}{T/\mathrm{K}}\right) + T/\mathrm{K} - 273.15\right) \qquad (3)$$

The pure component parameters for the ESD EoS are presented in Table 1.

Besides the binary interaction parameters, the data sets and deviations for total pressure and compositions of vapor and liquid phases are summarized in Table 2 for ESD EoS and in Table 3 for the NRTL and UNIQUAC equations. The calculations of the heptane + phenol parameters are based on LLE data from Vondracek taken from ref 12 and isobaric VLE data from Kolyuchkina et al. taken from ref 13 and our experimental photometric turbidity titration data, listed in the Supporting Information. For the heptane + phenol system the results of the binary calculation are diagrammed in Figure 2 for each applied model. The strong temperature dependence of the system is not described well with linear parameters. The isothermal VLE data from Gmehling et al.[13] are fitted together with our LLE data for the determination of the octane + phenol parameters. No phase

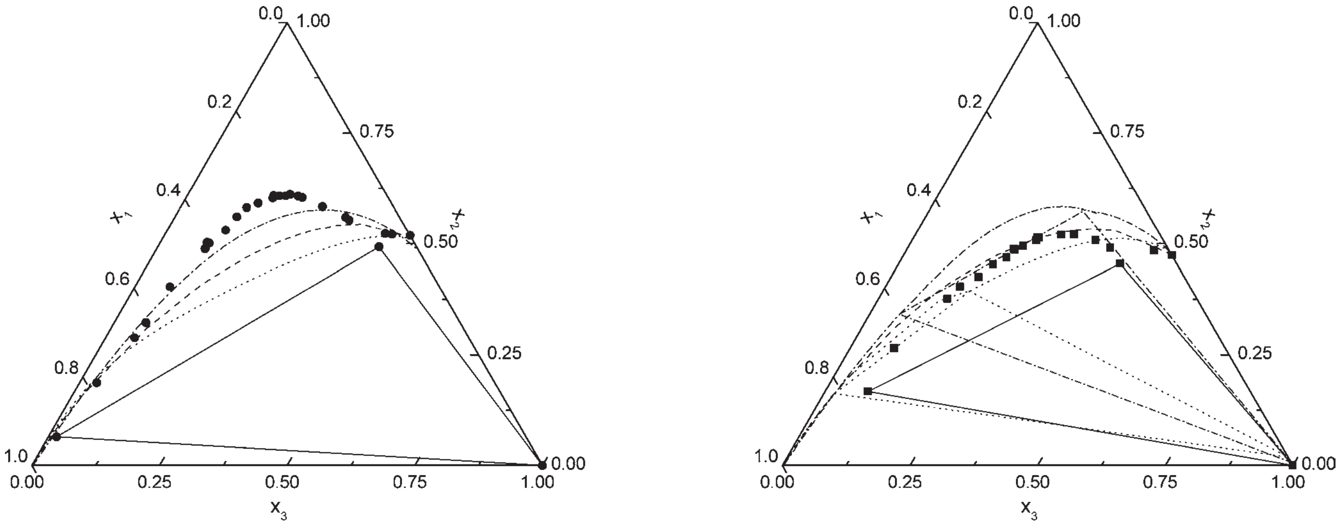

Figure 10. Results of prediction in the octane (1) + 3-cresol (2) + water (3) system. Experimental binodal curve and three-phase region: ●, solid line at 298.15 K; ■, solid line at 323.15 K. Predicted binodal curve and three-phase region: dashed−dotted line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

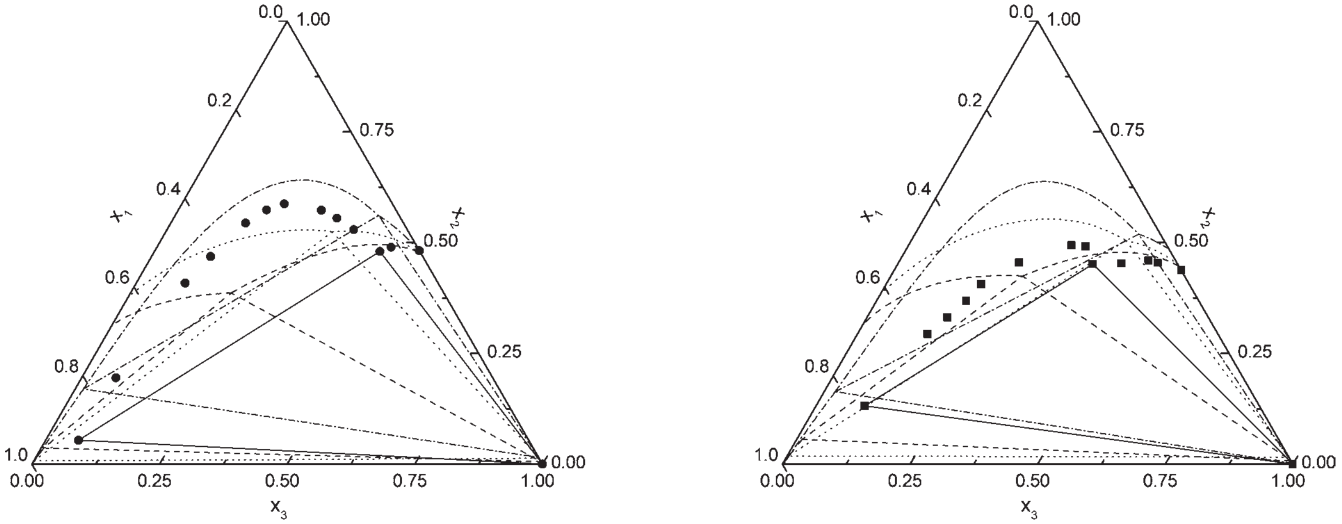

Figure 11. Results of prediction in the octane (1) + 4-cresol (2) + water (3) system. Experimental binodal curve and three-phase region: ●, solid line at 298.15 K; ■, solid line at 323.15 K. Predicted binodal curve and three-phase region: dashed−dotted line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

equilibrium data are available for the systems of heptane + 2-, 3-, or 4-cresol. Therefore VLE data at 298.15 K up to 363.15 K are predicted with the modified universal quasichemical functional-group activity coefficient (UNIFAC Dortmund) model.[14] The calculation of the octane + 4-cresol parameters is based on isobaric VLE data from Taylor and Wingard[15] and Hirata et al.[16]

The predictions of the investigated ternary system with the different UNIFAC models are not presented in this publication. The predictions with the original UNIFAC model (LLE parameter table)[17] are characterized by the wrong temperature dependence in the binary systems; the miscibility gap and the three-phase region are calculated too small. In contrast, a noticeably larger three-phase region and a phase separation in the binary systems aliphatic hydrocarbon + cresols are predicted with the modified UNIFAC model.

The ternary systems heptane + phenol + water and octane + phenol + water are specified by a binary phase split in the binary systems alkanes + phenol at 313.15 K, the experimental data as well as the prediction results for the two systems are presented in Figures 4 and 8, respectively. The experimental slopes of the binodal curve are predicted well with the ESD EoS. The excess Gibbs energy models NRTL and UNIQUAC describe the heterogeneous region as smaller than verified experimentally. The three-phase regions in both ternary systems are predicted too small with ESD EoS and too large with the NRTL and UNIQUAC approaches. Regarding the predictions at 333.15 K, where no phase separation occurs in the binary systems of heptane or octane + phenol, significant differences appear. Using the ESD EoS, the binodal curves are predicted very well; with the NRTL and UNIQUAC models a phase split is calculated for both binary aliphatic hydrocarbon + phenol systems. The insufficient adjustments to the experimental data are reflected in the ternary predictions. With the increasing number of adjusted parameters the quality of the binary correlation with the NRTL model improves; the results are presented in Figure 3 for the octane + phenol system. However, with the increasing number of parameters no continuous improvements are achieved regarding to the ternary predictions. The differences between experimental and predicted three-phase regions increase with rising temperature for all applied approaches.

The LLE in the ternary systems heptane + 2-cresol + water and octane + 2-cresol + water are represented in Figures 5 and 9, respectively. Comparing the prediction results, significant differences are visible between the applied approaches. The UNIQUAC predictions describe a smaller three-phase region than the experimental compositions in the ternary system heptane + 2-cresol + water, whereas the differences increase at higher temperatures. Aside from the differences in the three-phase prediction, the miscibility gaps are in close agreement at both temperatures. With the binary interaction parameters, the NRTL model and ESD EoS are not able to predict a three-phase separation at 298.15 K. By increasing temperature, both approaches calculate a three-phase region with a considerable deviation from the experimental results. The calculated miscibility gaps are too large at 323.15 K. The ESD EoS predictions in the system octane + 2-cresol + water characterize the experimental binodal curves as well as the three-phase regions with minor deviations at 298.15 K. Experimental and predicted results diverge at higher temperatures: the experimental temperature dependence cannot be predicted. Similar results are calculated with the NRTL model for the slope of the miscibility gap as well as the LLLE at both temperatures. The UNIQUAC prediction is reflected by a nonconformance, and a phase separation in the binary system octane + 2-cresol is calculated at 298.15 K. The three-phase regions are predicted too small at both temperatures with the UNIQUAC parameters.

In the heptane + 3-cresol + water system, the three-phase region is predicted slightly smaller than the experimental one at 298.15 K. The slope of the binodal curve is comparable to the experimental results; minor differences appear only with ESD EoS. However, on the basis of the binary interaction parameters the temperature dependence of the three-phase region and the binodal curve is not considered correctly in all predictions at 323.15 K (Figure 6). The predictions in the octane + 3-cresol + water are characterized by larger deviations between experimental and calculated data (Figure 10). All applied models are not able to determine a three-phase region with the given binary interaction parameters at 298.15 K. The predictions with the NRTL model indicate a three-phase region as well as the ESD EoS at 323.15 K, but the size and location of the three-phase regions are not reflected well. No three-phase region is predicted with the UNIQUAC model at the higher temperature. For the ternary predictions with the NRTL model, binary water + 3-cresol interaction parameters are used, published by Schmelzer et al.[18] The binary interaction parameters with an optimized α value, published by Klauck et al.[9] provide satisfactory binary results but yield disappointing results for both investigated ternary systems with 3-cresol.

Satisfactory results are achieved in the predictions of the heptane + 4-cresol + water system, represented in Figure 7. A three-phase region is calculated with the applied approaches at both temperatures. The miscibility gap as well as the sizes of the three-phase region is predicted too small by the NRTL and UNIQUAC model and too large with the ESD EoS. All applied models are not able to predict the temperature dependence with the used binary interaction parameters. The prediction results for the octane + 4-cresol + water system are represented in Figure 11. The three-phase region as well as the pathway of the binodal curve is determined to be too large at both temperatures with the ESD EoS. The calculations with the NRTL model are characterized by a phase separation in the binary octane + 4-cresol system. The three-phase regions are predicted to be too large at both temperatures. Similar results are predicted with the UNIQUAC model; a phase separation is forecasted in the octane + 4-cresol system at both temperatures. The size and location of the three-phase region deviates from the experimental results. Furthermore, the calculations with the applied binary interaction parameters are characterized by inverse temperature dependence.

CONCLUSIONS

The LLE were determined for two binary systems: heptane + phenol and octane + phenol. Furthermore, the LL(L)E for eight ternary systems were investigated at two different temperatures at atmospheric pressure: aliphatic hydrocarbon (heptane or octane) + phenol, 2-cresol, 3-cresol, or 4-cresol + water. The predictions in the ternary systems are based on binary interaction parameters, which were fitted on available VLE and LLE data as well as data predicted with the modified UNIFAC (Dortmund) model.

The investigated ternary systems offer a complex phase equilibrium behavior. None of the applied approaches is able to predict quantitatively the experimental behavior for all investigated systems at both temperatures. One reason for this result can be the limited binary database. However, the limits of the applied models are achieved probably in the description of such complex phase behavior. Satisfactory qualitative predictions are achieved for the systems heptane + 3- or 4-cresol + water with all applied approaches and for both ternary systems containing phenol with the ESD EoS.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental results of pure component densities, binary binodal curve measurements, ternary binodal curve, and three-phase region measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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