JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

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Liquid−Liquid Equilibria in Ternary Systems of Aromatic Hydrocarbons (Toluene or Ethylbenzene) + Phenols + Water

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Supporting Information

ABSTRACT: The liquid−liquid equilibria were determined in the ternary systems toluene + phenol or 2-cresol or 3-cresol or 4-cresol + water and ethylbenzene + phenol or 2-cresol or 3-cresol or 4-cresol + water at atmospheric pressure at temperatures of 298.15 K and 313.15 K or 323.15 K by photometric turbidity titration. The liquid−liquid equilibria in the ternary systems were predicted with the excess Gibbs energy models NRTL and UNIQUAC as well as the Elliott−Suresh−Donohue equation of state. Binary interaction parameters were calculated on the basis of available vapor−liquid and liquid−liquid equilibrium data and data predicted with the modified UNIFAC (Dortmund) model.

INTRODUCTION

The knowledge of liquid−liquid equilibria (LLE) permits accurate equipment configuration in the chemical industry. Especially the effective optimization of extraction processes requires comprehensive qualitative and quantitative phase equilibrium data. Experimental data are used to compare different prediction methods. The ESD EoS[1,2] (an equation of state proposed by Elliott, Suresh, and Donohue) predictions are compared with the widely used activity coefficient models NRTL[3] and UNIQUAC.[4] The investigated components are used by the pigment, drug, and synthetic industry.

EXPERIMENTAL SECTION

Materials. Phenol (Berlin Chemie, Berlin, Germany, purity > 98 % in mass) and the components 2-cresol, 3-cresol, and 4-cresol (Merck-Schuchardt, Hohenbrunn, Germany, with purity > 99 % in mass) were distilled twice in a Vigreux column at reduced pressure under a N_2 atmosphere and dried over Na_2SO_4. Toluene (Petrolchemisches Kombinat Schwedt, Germany) and ethylbenzene (Laborchemie Apolda, Germany) were obtained with purity p.a. Both aromatic hydrocarbons were also distilled in a Vigreux column at reduced pressure and stored over molecular sieves type 4A. Subsequently, the purities of all investigated components were verified by gas−liquid chromatography (GLC). The mass fractions of the substances were phenol (99.7 %), 2-cresol (> 99.1 %), 3-cresol (> 99.8 %), 4-cresol (99.8 %), toluene (> 99.8 %), and ethylbenzene (> 99.9 %). The measured physical properties vapor pressure and density are in agreement with literature data.[5,6] The densities are given in the Supporting Information. Deionized and distilled water was used.

Methods. The liquid−liquid equilibria were determined by photometric turbidity titration. Reliable results of binodal curve measurements were obtained in ternary systems of water + hydrocarbons + phenol and cresol,[7] cyclohexylamine,[8] and aniline[9] using this method. The experimental setup is based on a temperature-controlled glass vessel with magnetic stirrer. The configuration is completed by 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). A binary homogeneous mixture whose component masses are determined by weighing with an accuracy of ± 0.5 mg is prepared in the vessel. The third component water is added in small amounts of 0.02 mL by the automatic buret and dispensed within the homogeneous mixture via the low power ultrasonic generator. Intensive turbidity at the solubility limit is registered by the photometric light transmission measurements. The complete progress of the transmission measurement beyond two-phase occurrence is logged by a PC. The equilibrium compositions of the liquid phases in the binary and ternary systems are determined with an uncertainty of $\pm$ 0.003 $\text{mol}\cdot\text{mol}^{-1}$ and temperature uncertainty of ± 0.1 K. A detailed description of the measurement procedure as well as a scheme of photometric turbidity titration method are already published by Klauck et al.[8] The equilibrium data in the binary system of ethylbenzene + water are determined by Karl Fischer titration with an uncertainty of 1 % in mass of the measured value.

RESULTS AND DISCUSSION

Experimental Data. The liquid−liquid equilibria of eight ternary systems are determined at two different temperatures at atmospheric pressure. The experimental data are reported in the Supporting Information. The binodal curves indicate a type 2 character in all investigated systems agreeing to the classification of Treybal.[10]

The binary mixtures of aromatic hydrocarbons + phenols are homogeneous over the whole concentration and temperature range. By contrast, a large miscibility gap occurs in binary

Special Issue: John M. Prausnitz Festschrift

Received: March 10, 2010
Accepted: June 27, 2010
Published: August 06, 2010

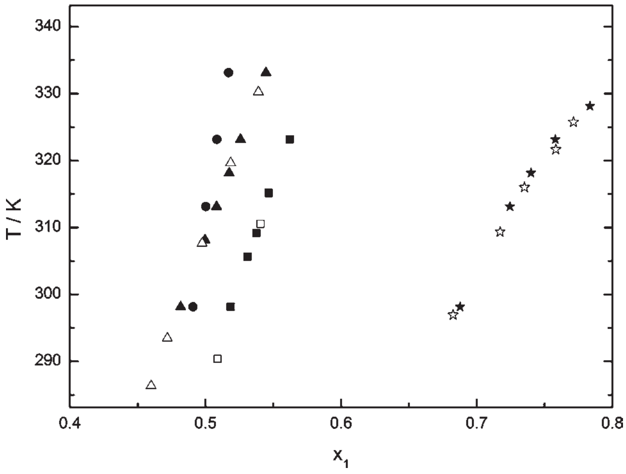

Figure 1. Temperature-dependent solubility of water (1) ★, in phenol (2) (this work); ●, in 2-cresol (2); ▲, in 3-cresol (2); ■, in 4-cresol (2) (ref 12); ☆, in phenol (ref 20); Δ, in 3-cresol (2); and □, in 4-cresol (2) (ref 21).

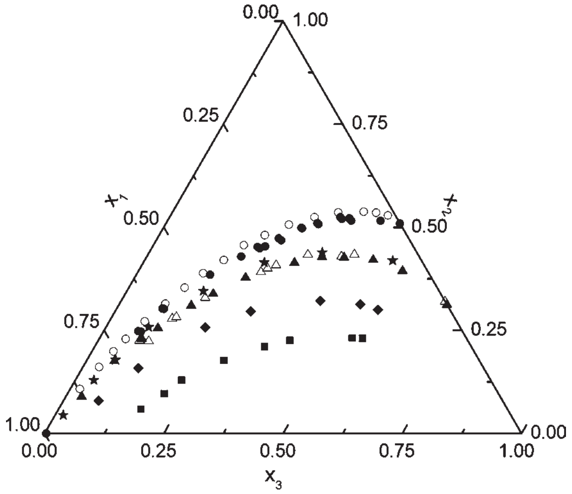

Figure 2. Experimental results in the systems of ▲, toluene (1) + phenol (2) + water (3); Δ, ethylbenzene (1) + phenol (2) + water (3); ●, toluene (1) + 2-cresol (2) + water (3); and ○, ethylbenzene (1) + 2-cresol (2) + water (3) at 298.15 K. Experimental results in the systems of toluene (1) + phenol (2) + water (3) at ◆, 423.15 K and ■, 473.15 K (ref 13) and experimental results in the system ethylbenzene (1) + phenol (2) + water (3) at ★, 298.15 K (ref 15).

mixtures of hydrocarbons + water, for example, toluene + water correlated by Tsonopoulos.[11] The phenols + water systems are characterized by a temperature-dependent miscibility gap. The solubility of water in phenol or cresols identifies a peculiarity within the temperature dependence, presented in Figure 1. The solubility of water in the phenols rises with increasing temperature. Phenol shows the strongest dependence followed by 4-cresol and 3-cresol. A significantly lower temperature dependence occurs when water is solved in 2-cresol. At 298.15 K, the water solubility is higher in 2-cresol than in 3-cresol. Nevertheless, the temperature influence of the binary system is not sufficient to change the course of the ternary binodal curves at 298.15 K. The experimental solubility data of water in phenol are given in the Supporting Information, and those of water in 2-, 3-, and 4-cresol were already published by Klauck et al.[12]

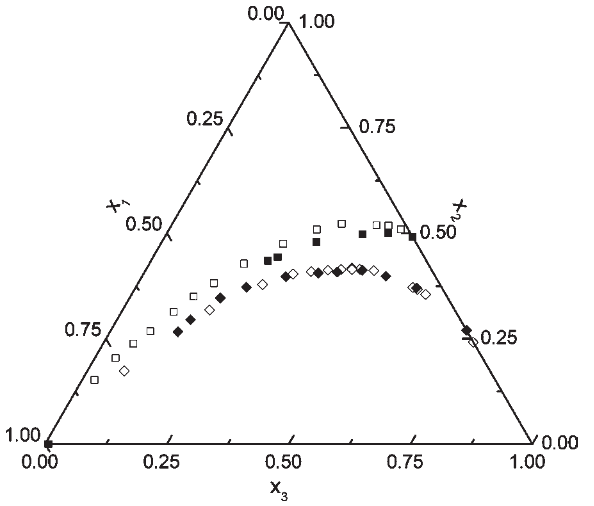

Figure 3. Experimental results in the systems of ◆, toluene (1) + phenol (2) + water (3) at 313.15 K; ◇, ethylbenzene (1) + phenol (2) + water (3); ■, toluene (1) + 2-cresol (2) + water (3); and □, ethylbenzene (1) + 2-cresol (2) + water (3) at 323.15 K.

Table 1. Pure Component Parameters for the ESD EoS

substance	references	c^a	$(\varepsilon_j/k)^b$	b^c	$\varepsilon_{HB}/RT_{crit}{}^d$	$\kappa_{AB}/\upsilon^{*e}$
			K	$cm^3 \cdot mol^{-1}$		
phenol	12	1.6503	415.407	34.391	3.0470	0.02936
2-cresol	12	1.1983	607.630	42.618	4.3269	0.00098
3-cresol	12	1.6317	444.525	41.836	3.3574	0.01201
4-cresol	12	2.0758	359.595	40.150	2.2174	0.1517
toluene	22	1.9707	332.752	44.238		
ethylbenzene	22	2.1223	333.658	42.242		
water	22	1.0053	427.254	9.411	4.0000	0.1000

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

All investigated ternary systems show a comparable temperature behavior: the miscibility gap decreases with increasing temperature. The comparative consideration of the investigated systems indicates a behavior independent of the aromatic hydrocarbon used in these experiments. The phenol systems are identified by the smallest miscibility gap at all temperatures. Experimental data in the cresol systems are only characterized by minor differences. The miscibility gap is increasing in following order: 4-cresol, 3-cresol, and 2-cresol.

The experimental data in the system toluene + phenol + water and ethylbenzene + phenol + water at 298.15 K are shown in Figure 2, along with data available in the literature. The equilibrium data at 423.15 K and 473.15 K provided by Hooper et al.[13] are characterized by a comparable slope of the binodal curve appropriate to the temperature. By contrast, the equilibrium compositions analyzed by GLC using the method of internal standard from Mohsen-Nia et al.[14] indicates significant discrepancies. The systematic consistency within the different ternary systems as well as the comparability with other literature data support the experimental data collected by photometric turbidity titration. The experimental data from Alvarez Gonzales et al.[15] at 298.15 K are presented in Figure 2 as well and indicate only minor differences to the determined data.

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

			k_{ij}^T	ΔP^a		
binary system	fitted data	k_{ij}^C	K^{-1}	%	Δy^b	Δx^b
toluene (1) + water (2)[c]		0.078281	0.00056063	11.29	0.0663	0.000576
toluene (1) + phenol (2)[d]		−0.010530	0.00001061	2.51	0.0070	
toluene (1) + 2-cresol (2)[d]		−0.035359	0.00032133	3.18	0.0084	
toluene (1) + 3-cresol (2)[d]		−0.014171	0.00011565	2.19	0.0042	
toluene (1) + 4-cresol (2)[d]		−0.008375	−0.00002098	2.20	0.0062	
ethylbenzene (1) + water (2)	this work, 11	0.072429	0.00059011			0.000129
ethylbenzene (1) + phenol (2)	17	−0.011808	−0.00000118	0.95	0.7675	
ethylbenzene (1) + 2-cresol (2)	UNIFAC prediction	−0.036891	0.00030194	3.79	0.0050	
ethylbenzene (1) + 3-cresol (2)	UNIFAC prediction	−0.017755	0.00011872	2.31	0.0121	
ethylbenzene (1) + 4-cresol (2)	UNIFAC prediction	−0.011982	0.00000811	1.83	0.0028	
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] $\Delta P = 100/n_p \cdot \Sigma(|P_{\text{calcld}} - P_{\text{exptl}}|/P_{\text{exptl}})$, where n_p is the number of data points. [b] $\Delta Z = 1/n_p \cdot \Sigma|Z_{\text{calcld}} - Z_{\text{exptl}}|$ where Z represents x or y. [c] Parameter taken from ref 8. [d] Parameter taken from ref 12.

Table 3. Parameters and Deviations of Binary Systems for the NRTL and UNIQUAC Model (Equation 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
toluene (1) + water (2)[c]		NRTL (α = 0.20)	1397.47	1983.05	−5.3412	6.0602	2.58	0.0146	0.000076
		UNIQUAC	1016.32	311.50	−3.6809	0.8284	2.74	0.0145	0.000068
toluene (1) + phenol (2)[d]		NRTL (α = 0.20)	857.14	−308.41	−4.3775	2.8430	1.83	0.0051	
		UNIQUAC	369.57	−146.32	−1.6642	0.9573	1.84	0.0051	
toluene (1) + 2-cresol (2)[d]		NRTL (α = 0.20)	942.67	−416.16	−5.9518	2.9683	0.78	0.0054	
		UNIQUAC	372.85	−191.68	−2.7563	1.6261	0.75	0.0054	
toluene (1) + 3-cresol (2)[d]		NRTL (α = 0.20)	909.79	−303.03	−5.1134	2.2854	2.01	0.0015	
		UNIQUAC	352.72	−149.49	−2.4085	1.3615	1.73	0.0015	
toluene (1) + 4-cresol (2)[d]		NRTL (α = 0.20)	443.83	−50.11	1.6730	−1.6607	1.46	0.0042	
		UNIQUAC	108.66	4.74	0.9399	−0.8258	1.48	0.0042	
ethylbenzene (1) + water (2)	this work, 11	NRTL (α = 0.20)	1455.50	2381.93	−5.0316	6.5386			0.000004
		UNIQUAC	1050.79	321.31	−3.4053	0.8353			0.000002
ethylbenzene (1) + phenol (2)	17	NRTL (α = 0.47)	818.36	−168.07	−3.6328	1.5458	0.98	0.7675	
		UNIQUAC	553.36	−231.97	−1.8855	0.7274	0.93	0.7675	
ethylbenzene (1) + 2-cresol (2)	UNIFAC prediction	NRTL (α = 0.20)	838.93	−317.40	1.1854	−0.9028	2.83	0.0056	
		UNIQUAC	364.15	−160.43	0.4017	−0.3691	2.96	0.0056	
ethylbenzene (1) + 3-cresol (2)	UNIFAC prediction	NRTL (α = 0.20)	802.72	−280.88	−0.1460	−0.1138	0.90	0.0009	
		UNIQUAC	340.36	−146.14	−0.0909	−0.0856	0.96	0.0010	
ethylbenzene (1) + 4-cresol (2)	UNIFAC prediction	NRTL (α = 0.20)	787.03	−276.30	−0.1130	−0.1126	0.29	0.0002	
		UNIQUAC	339.66	−145.83	−0.0818	−0.0896	0.02	0.00003	
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] $\Delta P = 100/n_p \cdot \Sigma(|P_{\text{calcld}} - P_{\text{exptl}}|/P_{\text{exptl}})$, where n_p is the number of data points. [b] $\Delta Z = 1/n_p \cdot \Sigma|Z_{\text{calcld}} - Z_{\text{exptl}}|$ where Z represents x or y. [c] Parameter taken from ref 8. [d] Parameter taken from ref 12. [e] Parameter taken from ref 7.

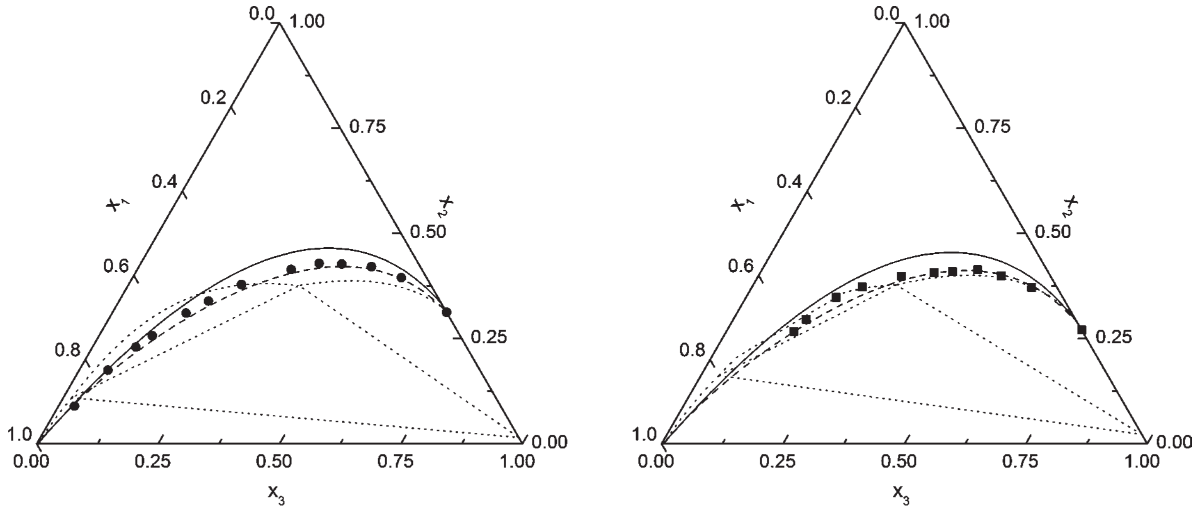

Figure 4. Results of prediction in the toluene (1) + phenol (2) + water (3) system. Experimental binodal curve at ●, 298.15 K and ■, 313.15 K; solid line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

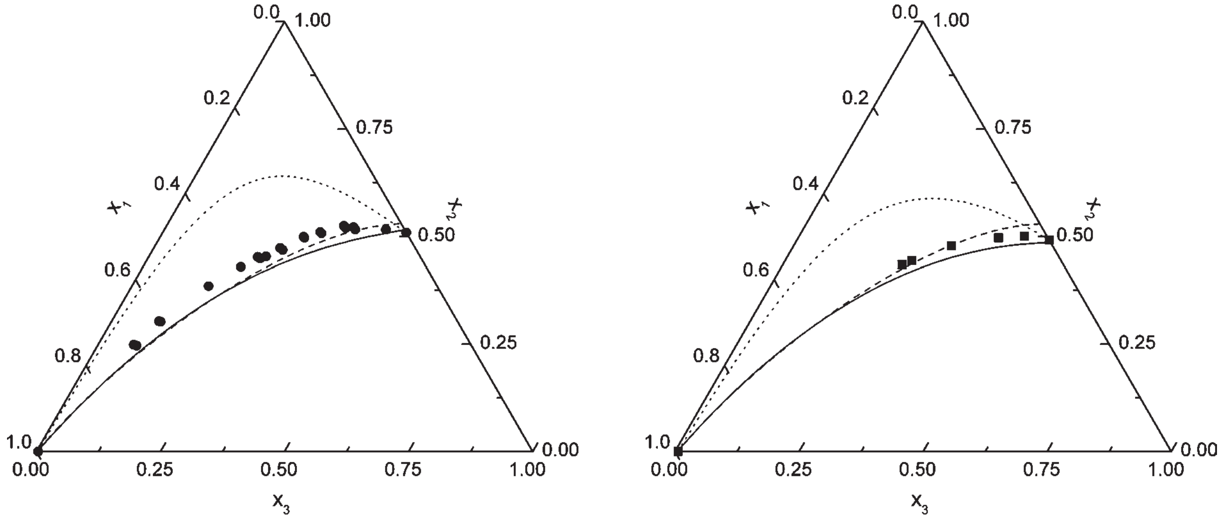

Figure 5. Results of prediction in the toluene (1) + 2-cresol (2) + water (3) system. Experimental binodal curve at ●, 298.15 K and ■, 323.15 K; solid line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

The comparison of the investigated hydrocarbons toluene and ethylbenzene indicates minor differences of binodal curves. The experimental results in the systems toluene + phenol + water and ethylbenzene + phenol + water are presented in Figure 2 as well as toluene + 2-cresol + water and ethylbenzene + 2-cresol + water at the same temperature. The miscibility gap increases minimally if ethylbenzene is used instead of toluene at the phenol system. By contrast, a significant difference between toluene and ethylbenzene is recognized in the 2-cresol systems. The influence of the hydrocarbon is amplified with rising temperature, reflected in Figure 3.

The 3-cresol systems are characterized by an initiating distinction between toluene and ethylbenzene at the higher temperature, while the 4-cresol and the phenol systems show a comparable behavior at both temperatures. The water-rich phase consists nearly of pure water in all investigated ternary systems. Therefore, no experimental data were determined. To compare the calculated and experimental tie-lines, the compositions in the water-rich phase were estimated based on binary solubility data.

Correlations and Predictions. Predictions of the ternary phase behavior are based on binary interaction parameters for all applied approaches. The binary interaction parameters of the activity coefficient models are assumed to be linearly temperature-dependent (eq 1)

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

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.[16] was used

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

where P stands for pressure; y represents the vapor mole fraction; x' and x'' are the mole fractions of the different phases at

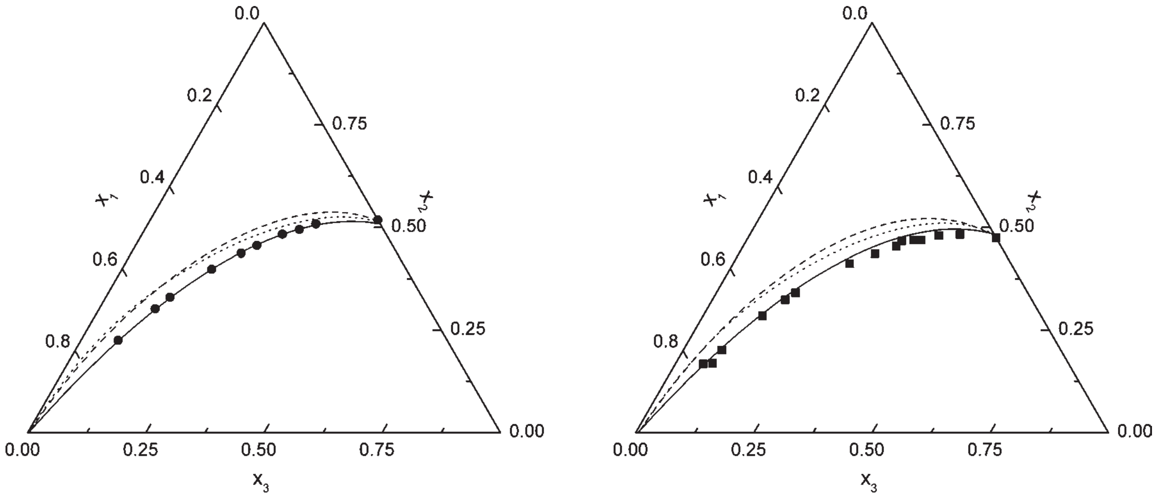

Figure 6. Results of prediction in the toluene (1) + 3-cresol (2) + water (3) system. Experimental binodal curve at ●, 298.15 K and ■, 323.15 K; solid line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

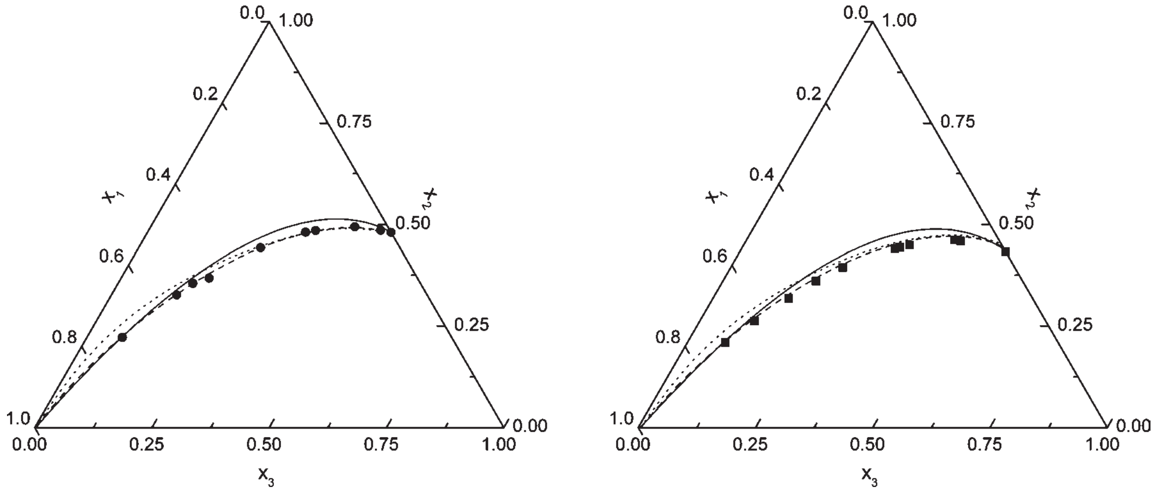

Figure 7. Results of prediction in the toluene (1) + 4-cresol (2) + water (3) system. Experimental binodal curve at ●, 298.15 K and ■, 323.15 K; solid line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

liquid−liquid equilibrium; and Π_i is a weighting factor. The binary ESD EoS parameters k_{ij} are assumed to depend on temperature (eq 3)

$$k_{ij} = k_{ij}^C + k_{ij}^T(T - 273.15\ \mathrm{K}) \qquad (3)$$

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

The binary interaction parameters are fitted simultaneously to available binary equilibrium data and are summarized for the ESD EoS in Table 2 and the models NRTL and UNIQUAC in Table 3. For the system ethylbenzene + water, data correlated by Tsonopoulos[11] are combined with our experimental solubility data (Supporting Information). The parameters for ethylbenzene + phenol are based on isothermal VLE data from Anderko.[17] No phase equilibrium data are available for the systems of ethylbenzene + 2-, 3-, or 4-cresol. Therefore, VLE data at 323.15 K up to 363.15 K are predicted with the modified UNIFAC model[18] in steps of 10 K.

The predictions of the investigated ternary system with the different UNIFAC models are not presented in this publication. The binary predictions in the systems of phenols + water are characterized by wrong temperature dependence with the original UNIFAC model,[19] while the modified UNIFAC model[18] predicts a noticeably larger miscibility gap. The deviations from the experimental data are continued in the ternary predictions as well; therefore, no ternary predictions are reported in this publication.

In the system toluene + phenol + water (Figure 4), the binodal curves predicted with the UNIQUAC model match very well at both investigated temperatures. The miscibility gaps are predicted too large with the ESD EoS at both temperatures. The largest deviations between experimental and predicted data occur with the NRTL model, and a three-phase region is calculated at 298.15 K and 313.15 K as well. Comparable results for the UNIQUAC model and the ESD EoS were received for the ethylbenzene + phenol + water system, presented in Figure 8. The prediction with the NRTL model results in three liquid phases at 298.15 K and two liquid phases at 323.15 K.

Significant differences appear in the prediction of the system toluene + 2-cresol + water diagrammed in Figure 5. With the used binary interaction parameters, UNIQUAC and ESD EoS are not able to describe the experimental slope of the miscibility

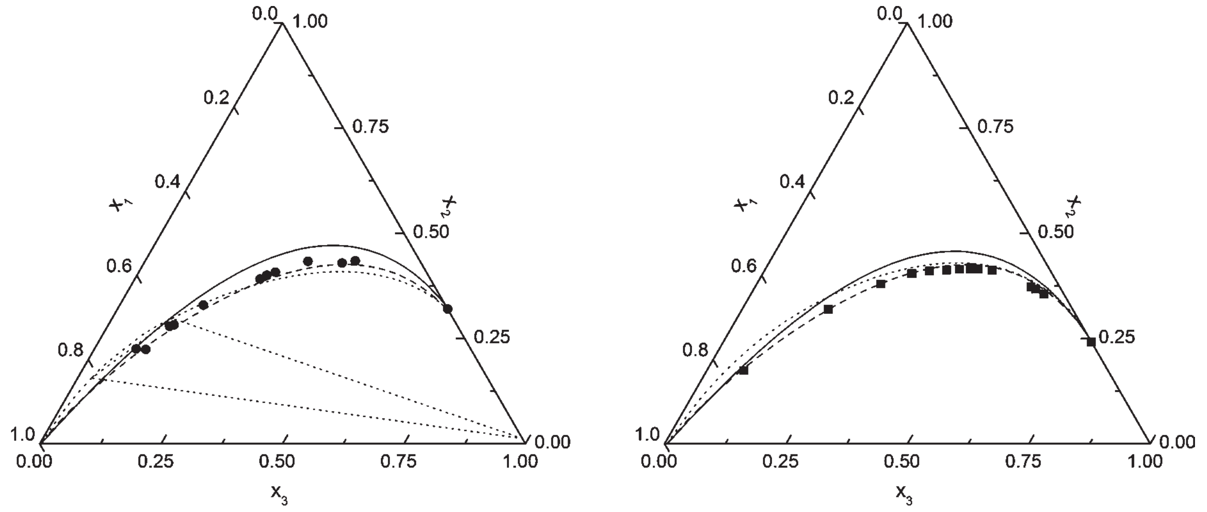

Figure 8. Results of prediction in the ethylbenzene (1) + phenol (2) + water (3) system. Experimental binodal curve at ●, 298.15 K and ■, 323.15 K; solid line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

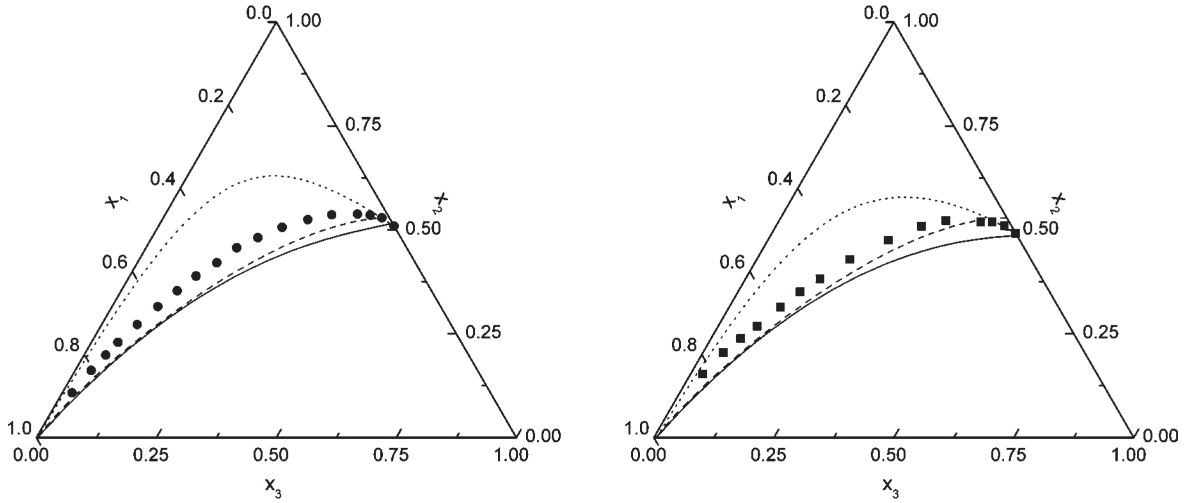

Figure 9. Results of prediction in the ethylbenzene (1) + 2-cresol (2) + water (3) system. Experimental binodal curve at ●, 298.15 K and ■, 323.15 K; solid line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

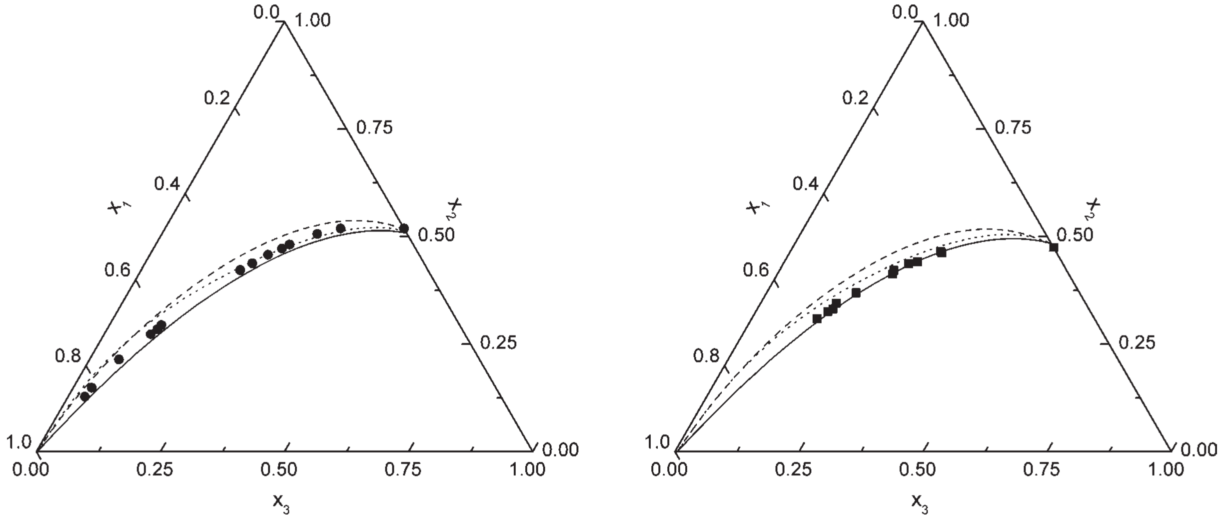

Figure 10. Results of prediction in the ethylbenzene (1) + 3-cresol (2) + water (3) system. Experimental binodal curve at ●, 298.15 K and ■, 323.15 K; solid line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

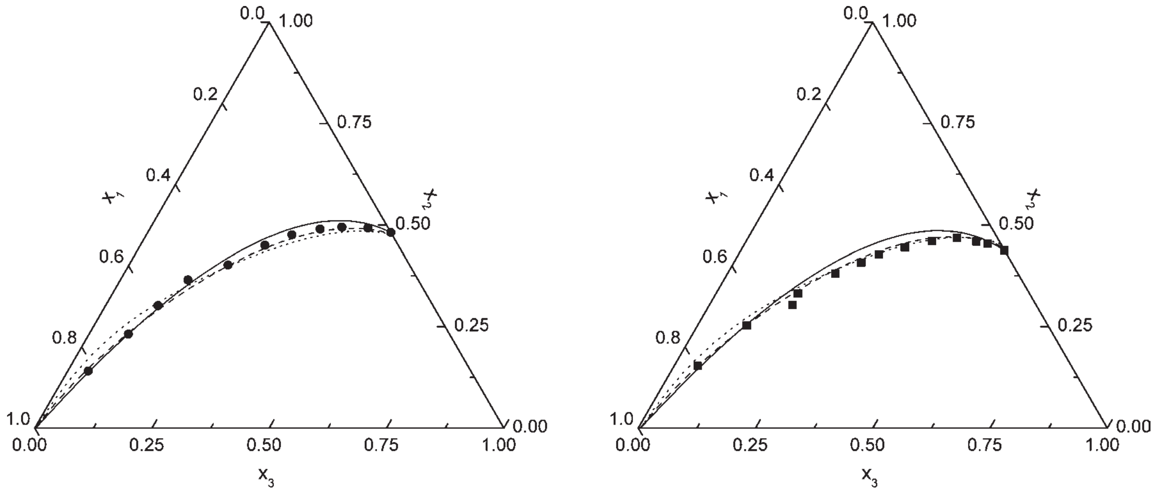

Figure 11. Results of prediction in the ethylbenzene (1) + 4-cresol (2) + water (3) system. Experimental binodal curve at ●, 298.15 K and ■, 323.15 K; solid line, ESD EoS; dashed line, UNIQUAC model; dotted line, NRTL model.

Table 4. Summarized Deviations between Experimental and Calculated Liquid Composition for ESD EoS, UNIQUAC, and NRTL

	ESD EoS		UNIQUAC		NRTL	
system	$\Delta x_{\text{organic}}$	Δx_{water}	$\Delta x_{\text{organic}}$	Δx_{water}	$\Delta x_{\text{organic}}$	Δx_{water}
toluene (1) + phenol (2) + water (3)	0.0154	0.0021	0.0064	0.0094		
toluene (1) + 2-cresol (2) + water (3)	0.0142	0.0006	0.0107	0.0008	0.0548	0.0014
toluene (1) + 3-cresol (2) + water (3)	0.0040	0.0031	0.0228	0.0089	0.0175	0.0114
toluene (1) + 4-cresol (2) + water (3)	0.0109	0.0076	0.0040	0.0044	0.0085	0.0072
ethylbenzene (1) + phenol (2) + water (3)	0.0259	0.0228	0.0100	0.0089		
ethylbenzene (1) + 2-cresol (2) + water (3)	0.0217	0.0006	0.0152	0.0008	0.0350	0.0013
ethylbenzene (1) + 3-cresol (2) + water (3)	0.0255	0.0027	0.0371	0.0069	0.0284	0.0094
ethylbenzene (1) + 4-cresol (2) + water (3)	0.0080	0.0071	0.0042	0.0042	0.0070	0.0067
mean	0.0157	0.0058	0.0138	0.0055		

gap at both temperatures correctly. Substantial difficulties occur with the binodal curve predicted with the NRTL model. The miscibility gap is modeled too large at both temperatures. A comparison to the ethylbenzene + 2-cresol + water system discloses similar problems within the predictions (Figure 9). Due to the comparable predictions for toluene and ethylbenzene with the NRTL model it can be concluded that the binary 2-cresol + water interaction parameters cause the disappointing predictions.

The liquid−liquid equilibria in the ternary system toluene + 3-cresol + water and ethylbenzene + 3-cresol + water are represented in Figures 6 and 10. The UNIQUAC predictions describe a larger miscibility gap than the investigated experimental compositions, whereas the differences increase at higher temperature. Slightly better calculations are achieved with the NRTL model for both ternary systems. The ternary systems with 3-cresol are predicted with the binary water + 3-cresol interaction parameters published by Schmelzer et al.[7] The calculation in this binary system indicates a higher deviation between experimental and calculated liquid and vapor composition and as well total pressure with $\alpha = 0.2$ compared to the optimized α value at the binary interaction parameters published by Klauck et al.[12] The predictions with this binary NRTL parameter (ref 12) yields disappointing results at both investigated ternary 3-cresol systems, comparable with the 2-cresol results represented in Figures 5 and 9.

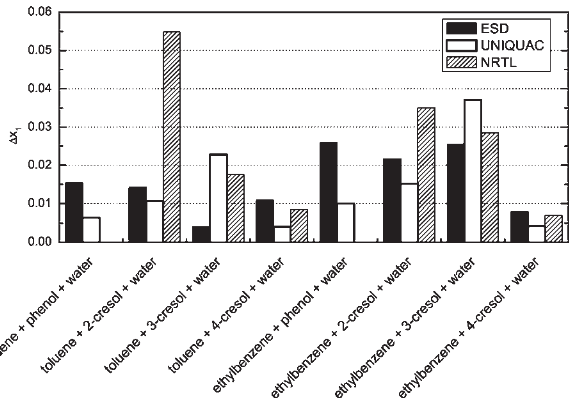

Figure 12. Deviations between experimental and calculated liquid composition for ESD EoS, UNIQUAC, and NRTL (organic phase).

The ESD EoS results characterize the binodal curve excellently with tight tolerances at both temperatures at the ternary systems.

The predictions in the systems toluene + 4-cresol + water and ethylbenzene + 4-cresol + water are in very good agreement with the experiment for all used models. The UNIQUAC and NRTL models describe the experimental behavior with a high accuracy at the whole course at both temperatures. The prediction with the ESD EoS model shows minimal deviations with the decreasing 4-cresol mole fraction within the ternary composition. Figures 7 and 11 diagram the experimental data at both temperatures as well as the prediction results.

CONCLUSIONS

The liquid−liquid equilibria for the eight ternary systems were determined for two temperatures at atmospheric pressure: toluene + phenol or 2-cresol or 3-cresol or 4-cresol + water and ethylbenzene + phenol or 2-cresol or 3-cresol or 4-cresol + water. Binary interaction parameters of simultaneously fitted available VLE and LLE data as well as data predicted with modified UNIFAC (Dortmund) provide the basis for the ternary predictions. Overall, with the applied models UNIQUAC and ESD EoS, acceptable deviations are achieved between experimental and predicted results, represented in Table 4 and Figure 12. The very small mole fractions in the water-rich phase reduce the deviation between the estimated experimental and simulated data. Therefore, the error analysis is related to the organic phase exclusively (Figure 12). The mean deviation is for the UNIQUAC model a mole fraction less than 0.014 and for the ESD EoS a mole fraction of 0.016 for all investigated systems. The largest deviations between experimental and calculated data are obtained in the NRTL predictions. Besides the achieved deviations for the systems containing cresols, the three-phase calculation in both systems with phenol does not allow a deviation summary for the NRTL model. The most balanced predictions are achieved with the ESD EoS model, and there are no deviations of the mole fraction that are greater than 0.026.

ASSOCIATED CONTENT

Supporting Information. Experimental results of ternary binodal curve measurements, solubilities of ethylbenzene or phenol in water, and pure component densities. This material is available free of charge via the Internet at http://pubs.acs.org.

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