JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Vapor−Liquid Equilibria in Ternary Systems of Toluene or Octane + Phenols + Water

Antje Martin, Mandy Klauck, Andreas Grenner, René Meinhardt, Klaus Taubert, Annett Precht, Diana Martin, and Jürgen Schmelzer*

Department of Chemical Engineering, Hochschule für Technik und Wirtschaft Dresden—University of Applied Sciences, Friedrich-List-Platz 1, 01069 Dresden, Germany

Supporting Information

ABSTRACT: The isothermal vapor−liquid equilibrium data are presented for the systems toluene or octane + phenol + water, toluene or octane + 2-cresol + water, toluene or octane + 3-cresol + water, and toluene + 4-cresol + water at two different temperatures and reduced pressures. The experimental data were determined in a modified Röck and Sieg type circulation still and were compared with the predictions of the activity coefficient models nonrandom two-liquid (NRTL) and universal quasichemical (UNIQUAC) models as well as the Elliott−Suresh−Donohue equation of state (ESD EoS).

INTRODUCTION

Comprehensive qualitative and quantitative phase equilibrium data provide the basis for the design and development of rectification processes. The knowledge of the composition of liquid and vapor phase as well as pressure and temperature dependence enables a comparison and a judgment of different prediction methods. In this work the experimental vapor−liquid equilibrium (VLE) data are compared with the predicted results of the nonrandom two-liquid (NRTL)[1] and universal quasichemical (UNIQUAC)[2] models and the Elliott−Suresh−Donohue equation of state (ESD EoS).[3,4] The experimental data were determined in a dynamic Röck and Sieg type circulation still. The systems toluene or octane + phenol + water, toluene + 2-cresol + water, toluene or octane + 3-cresol + water, and toluene + 4-cresol + water were measured at (333.15 and 363.15) K, the system octane + 2-cresol + water was determined at (333.15 and 353.15) K. The experimental vapor−liquid tie lines have a similar orientation in all investigated systems, although there are proven differences between toluene and octane in the liquid−liquid equilibrium behavior of the ternary systems of hydrocarbons + phenols + water.[5,6]

EXPERIMENTAL SECTION

Materials. The components phenol, 2-cresol, 3-cresol, 4-cresol, and octane were purchased from Merck-Schuchardt, Hohenbrunn, Germany, with mass purities of 0.99. Toluene was obtained from Petrolchemisches Kombinat Schwedt, Germany, with purity (p.a. grade). 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 purity verification by gas−liquid chromatography (GLC) resulted as follows in mass fraction: phenol (> 0.997), 2-cresol (> 0.991), 3-cresol (> 0.998), 4-cresol (> 0.998), toluene (> 0.998), and octane (> 0.995). The pure component density measurements are in agreement with the published data, listed in the Supporting Information. Deionized and distilled water was used in all experiments.

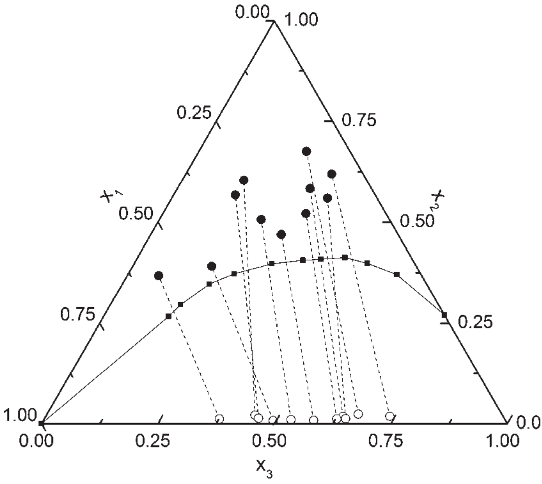

Figure 1. Experimental VLE data of toluene (1) + phenol (2) + water (3) at 333.15 K. ●, liquid composition; ○, vapor composition; −■−, experimental binodal curve at 313.15 K taken from ref 5.

Methods. The determination of the isothermal VLE data were realized in a modified Röck and Sieg type circulation still. The apparatus is made up of the following components: a modified glass circulation still, a temperature measuring module consisting of a calibrated platinum resistance thermometer and a computer system, a high accuracy pressure control composed of a pressure transducer and signal conditioner, and two magnetic valves. The ternary liquid mixture is prepared in the boiling flask of the circulation still and

Received: August 27, 2010
Accepted: January 19, 2011
Published: February 28, 2011

heated until boiling. The two magnetic valves are used to adjust the pressure and therefore indirectly the appropriate boiling temperature. After reaching the steady equilibrium state at the desired temperature, the corresponding pressure is recorded, and samples of liquid and condensed vapor are taken. A detailed description of the control and measurement equipment is published by Schmelzer et al.[7]

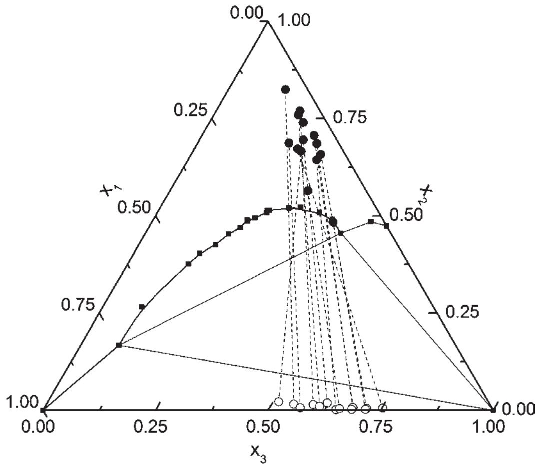

Figure 2. Experimental VLE data of octane (1) + 3-cresol (2) + water (3) at 333.15 K. ●, liquid composition; ○, vapor composition; −■−, experimental binodal curve and three-phase region at 323.15 K taken from ref 6.

Table 1. Pure Component Parameters for the ESD EoS

substance	refs	c^a	ε_j/k^b K	b^c $\mathrm{cm^3 \cdot mol^{-1}}$	$\varepsilon_{HB}/RT_{crit}{}^d$	κ_{AB}/v^{*e}
phenol	10	1.6503	415.407	34.391	3.0470	0.02936
2-cresol	10	1.1983	607.630	42.618	4.3269	0.00098
3-cresol	10	1.6317	444.525	41.836	3.3574	0.01201
4-cresol	10	2.0758	359.595	40.150	2.2174	0.1517
toluene	12	1.9707	332.752	44.238		
octane	12	2.2842	285.211	54.157		
water	12	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.

The analysis of the liquid and vapor samples are carried out with a combination of two methods. Densities of mixtures with a constant ratio of phenols + water were measured over the entire concentration range for the systems toluene + phenol, 2-cresol, 3-cresol, or 4-cresol + water and octane + 2-cresol or 3-cresol + water. With the aid of these results, parameters for lines of constant density were calculated. Then the composition of vapor or liquid phase can be calculated from the water content and the density of the sample. The content of water is determined by Karl Fischer titration (716 DMS Titrino, Deutsche Metrohm, Filderstadt) with an uncertainty of 1 % in mass of the measured value. The density is measured using a vibration tube densimeter (DMA 58, Anton Paar, Austria). The overall uncertainty of the composition can be specified with 0.002 $\mathrm{mol \cdot mol^{-1}}$. The analyses in the octane + phenol + water system are based on a combination of Karl Fischer titration and a quantitative conversion with bromine[8] for the content of phenol. 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. With this method the uncertainty can be specified with 0.005 $\mathrm{mol \cdot mol^{-1}}$ for composition. The uncertainties for the VLE data are 0.03 K for the temperature and 0.06 kPa for pressure.

RESULTS AND DISCUSSION

Experimental Data. The vapor−liquid equilibria of seven ternary systems are determined at two different temperatures; the experimental data are summarized in the Supporting Information. All investigated ternary systems indicate a similar VLE behavior. Despite the obvious differences in the liquid−liquid(−liquid) equilibrium,[5,6] the course of the experimental tie lines between vapor and liquid

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

binary system	k_{ij}^C	k_{ij}^T $\mathrm{K^{-1}}$	k_{ij}^{TT} $\mathrm{K^{-1}}$	ΔP^a %	Δy^b	Δx^b
toluene (1) + water (2)[c]	0.078281	0.00056063		11.3	0.0663	0.00058
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	
octane (1) + water (2)[c]	0.154728	0.00066375		5.97	0.0176	0.0003
octane (1) + phenol (2)[e]	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	
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] $\Delta P = 100/n_p \cdot \sum(|P_{calcd} - P_{exptl}|/P_{exptl})$, where n_p is number of data points. [b] $\Delta Z = 1/n_p \cdot \sum|Z_{calcd} - Z_{exptl}|$, where Z represents x or y. [c] Parameter taken from ref 9. [d] Parameter taken from ref 10. [e] Parameter taken from ref 6.

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

binary system	model	C_{12}^{C} / K	C_{21}^{C} / K	C_{12}^{T}	C_{21}^{T}	ΔP[a] / %	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	
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)[e]	NRTL (α = 0.25)	378.48	405.11	−0.2610	1.4775	2.30	0.0066	0.0748
	UNIQUAC	282.11	−42.67	0.5226	−0.1023	1.85	0.0073	0.0778
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	
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)[f]	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] $\Delta P = 100/n_p \cdot \sum(|P_{\mathrm{calcd}} - P_{\mathrm{exptl}}|/P_{\mathrm{exptl}})$, where n_p is number of data points. [b] $\Delta Z = 1/n_p \cdot \sum|Z_{\mathrm{calcd}} - Z_{\mathrm{exptl}}|$, where Z represents x or y. [c] Parameter taken from ref 9. [d] Parameter taken from ref 10. [e] Parameter taken from ref 6. [f] Parameter taken from ref 11.

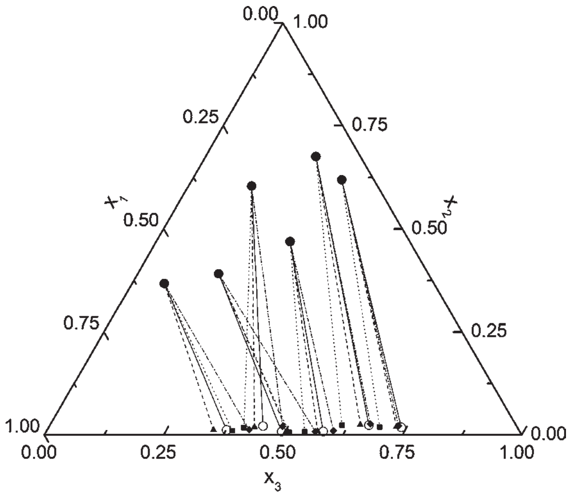

Figure 3. Selected experimental VLE data of toluene (1) + phenol (2) + water (3) at 333.15 K. ●, liquid composition; ○, vapor composition; solid line, experimental tie-line. Calculated vapor composition and tie lines: ♦, and dashed−dotted line, ESD EoS; ▲, and dashed line, UNIQUAC model; ■, and dotted line, NRTL model.

compositions is not affected. The experimental VLE data at 333.15 K and the binodal curve at 313.15 K for the system toluene + phenol + water are presented in Figure 1. For comparison, Figure 2 shows the results for the system octane + 3-cresol + water, the miscibility gap with three-phase region at 323.15 K, and the vapor−liquid tie lines at 333.15 K. The vapor compositions have a high amount of water and toluene or octane in all measured systems corresponding to the composition of the binary heteroazeotropic point of water + toluene or octane, respectively. Most of the investigated liquid compositions were homogeneous; only few heterogeneous liquid compositions were analyzed.

Correlations and Predictions. The predictions of the ternary VLE data with the ESD EoS ($\phi-\phi$ approach) and the excess Gibbs energy models UNIQUAC and NRTL ($\gamma-\phi$ approach; vapor phase ideal) are based on binary interaction parameters presented by Martin et al.,[6] Klauck et al.,[9,10] and Schmelzer et al.[11] The binary interaction parameters for the activity coefficient models are supposed to be linearly temperature-dependent (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 binary ESD EoS parameters k_{ij} are assumed

Table 4. Deviations between Experimental and Calculated Total Pressures and Vapor Compositions

	no. data points		ESD EoS		UNIQUAC		NRTL	
			ΔP^a		ΔP^a		ΔP^a	
system	P	y	%	Δy^b	%	Δy^b	%	Δy^b
toluene + phenol + water	22	22	8.4	0.018	4.4	0.010	5.6	0.020
toluene + 2-cresol + water	28	28	2.6	0.013	3.2	0.005	14.6	0.034
toluene + 3-cresol + water	22	12	4.1	0.021	5.9	0.034	4.0	0.031
toluene + 4-cresol + water	21	21	5.6	0.028	2.9	0.031	3.4	0.043
octane + phenol + water	28	28	10.2	0.057	9.7	0.063	10.2	0.062
octane + 2-cresol + water	23	21	12.3	0.037	4.7	0.029	14.3	0.045
octane + 3-cresol + water	29	27	7.9	0.046	8.1	0.060	10.2	0.058
total	173	159	7.3	0.033	5.7	0.034	9.3	0.044

[a] $\Delta P = 100/n_p \cdot \sum(|P_{\text{calcd}} - P_{\text{exptl}}|/P_{\text{exptl}})$. [b] $\Delta y = 1/n_p \cdot \sum|y_{\text{calcd}} - y_{\text{exptl}}|$, where n_p is number of data points.

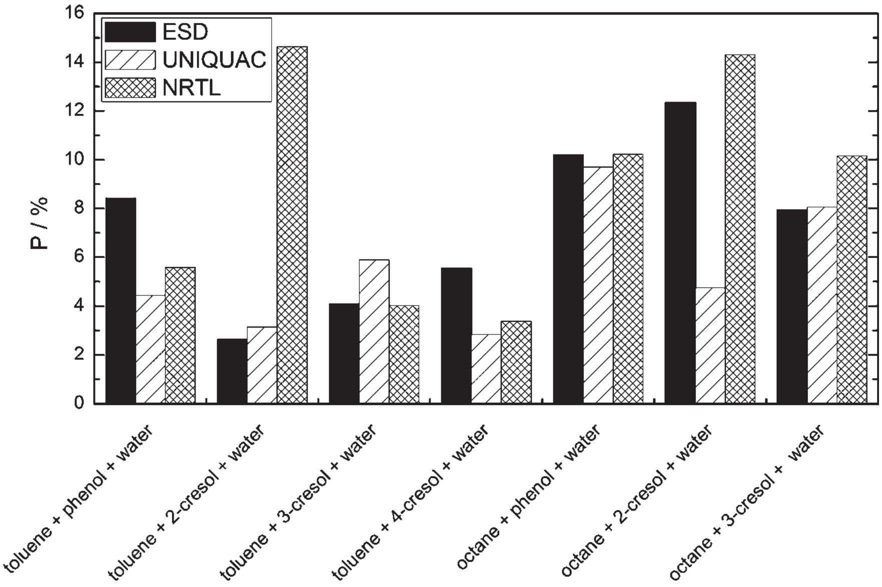

Figure 4. Relative deviations of experimental and calculated total pressures for the ternary systems.

to depend linearly on temperature (if $k_{ij}^{TT} = 0$) or to have an extended temperature function (eq 2)

$$k_{ij} = k_{ij}^{C} + k_{ij}^{T}/\text{K}^{-1}(T/\text{K} - 273.15) + k_{ij}^{TT}/\text{K}^{-1}\left(T/\text{K}\ln\left(\frac{298.15}{T/\text{K}}\right) + T/\text{K} - 273.15\right) \tag{2}$$

The pure component parameters for the ESD EoS are represented in Table 1. For ESD EoS the binary parameters are summarized in Table 2 including the deviations between experimental and calculated values for total pressure and compositions of vapor and liquid phases. The binary interaction parameters for the NRTL and UNIQUAC equations are shown in Table 3. The same parameter sets were used to predict liquid−liquid(−liquid) equilibria in ternary systems[5,6] as well.

Using the system toluene + phenol + water at 333.15 K as an example, the course of the selected experimental and predicted tie lines is presented in Figure 3. The vapor compositions for this system are calculated with following deviations in mole fractions (Table 4): 0.010 for the UNIQUAC model, 0.018 for the ESD EoS, and 0.020 for the NRTL model. However, the selected tie lines show few significant differences for single data points dependent from the vapor compositions and the applied prediction methods. The differences between experimental and with NRTL predicted vapor composition are reduced with an increasing concentration of toluene in the vapor phase. Directly opposed behavior indicates the prediction with the ESD EoS for the selected tie lines; the deviations are raised with an increasing concentration of toluene in the vapor composition. The most uniform deviations for the selected vapor compositions are obtained with the UNIQUAC model.

The deviations of predicted and measured ternary VLE data are summarized in Table 4; the deviations are diagrammed for the total pressure (Figure 4) and for the vapor composition (Figure 5). The comparison of the prediction results shows clear differences: the deviations for the ternary systems containing toluene are noticeably lower compared to the systems containing octane. Satisfactory results for the vapor compositions are performed for all investigated systems and models. The VLE

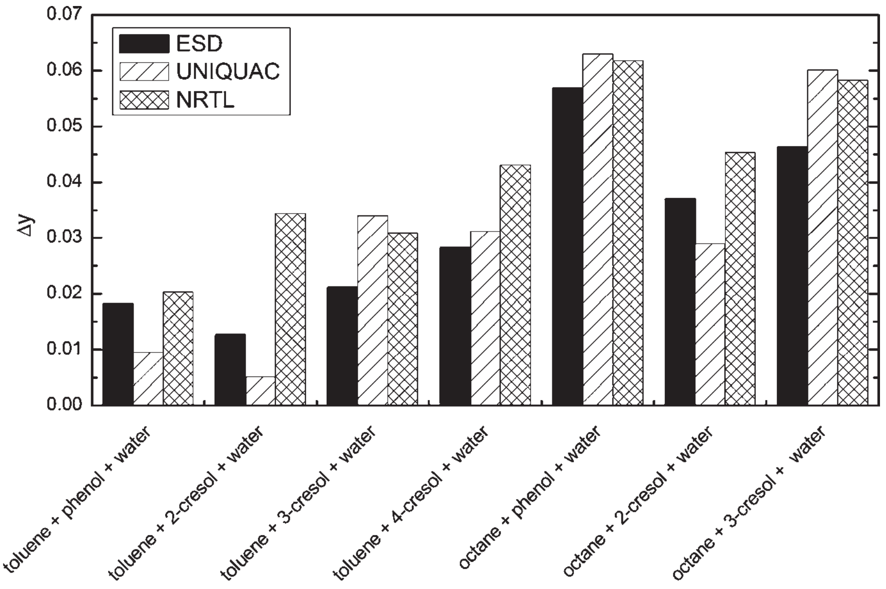

Figure 5. Absolute deviations of experimental and calculated vapor compositions for the ternary systems.

data in the system toluene + 2-cresol + water are calculated with the lowest deviation of 0.005 mole fraction with the UNIQUAC model. By contrast, the maximum deviation of 0.063 mole fraction in the vapor composition is obtained with the UNIQUAC model for the system octane + phenol + water. The average deviation for the predicted vapor composition (given as mole fraction) is 0.033 for the ESD EoS, 0.034 for the UNIQUAC model, and 0.044 for the NRTL model for all investigated systems.

The prediction of the total pressure is characterized by noticeable differences for the investigated ternary systems. The best results are obtained for the system toluene + 2-cresol + water with a deviation of 2.6 % for the total pressure using the ESD EoS. The NRTL predictions indicate the largest deviation with 14.6 %, respectively 14.3 %, for the total pressure in both ternary systems containing 2-cresol, although an optimized non-randomness parameter was used. The calculation of liquid—liquid(—liquid) equilibria[5,6] identified a problematic prediction with the applied NRTL parameters for the system 2-cresol + water. In summary, the deviations of the total pressure for all systems are calculated with 5.7 % for the UNIQUAC model, 7.3 % for the ESD EoS, and 9.3 % for the NRTL model.

■ CONCLUSIONS

The vapor—liquid equilibria were investigated for the systems toluene or octane + phenol + water, toluene or octane + 2-cresol + water, toluene or octane + 3-cresol + water, and toluene + 4-cresol + water at two different temperatures and reduced pressures. The predictions of the VLE in the ternary systems are based on given binary interaction parameters for each applied model, which are also used to calculate the liquid—liquid(—liquid) equilibria. Summarizing the predictions, the most reliable results are obtained with the UNIQUAC model followed by the ESD EoS for the investigated systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental results of pure component densities and VLE measurements of ternary systems. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +49-351-462-2777. Fax: +49-351-462-3228. E-mail: schmelzer@mw.htw-dresden.de.

■ REFERENCES

(1) Renon, H.; Prausnitz, J. M. Local composition in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(2) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the Gibbs energy of partly or complete miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(3) Elliott, J. R.; Suresh, S. J.; Donohue, M. S. A simple equation of state for non-spherical and associating molecules. *Ind. Eng. Chem. Res.* **1990**, *29*, 1476–1485.

(4) Suresh, S. J.; Elliott, J. R. Multiphase equilibrium analysis via a generalized equation of state for associating mixtures. *Ind. Eng. Chem. Res.* **1992**, *31*, 2783–2794.

(5) Martin, A.; Klauck, M.; Taubert, K.; Precht, A.; Meinhardt, R.; Schmelzer, J. Liquid-liquid equilibria in ternary systems of aromatic hydrocarbons (toluene or ethylbenzene) + phenols + water. *J. Chem. Eng. Data* **2010**, DOI: 10.1021/je100069q.

(6) Martin, A.; Klauck, M.; Grenner, A.; Meinhardt, R.; Martin, D.; Schmelzer, J. Liquid-liquid equilibria in ternary systems of aliphatic hydrocarbons (heptane or octane) + phenols + water. *J. Chem. Eng. Data* **2010**, DOI: 10.1021/je1007923.

(7) Schmelzer, J.; Niederbröker, H.; Lerchner, J. Computer-controlled equipment for the dynamic measurement of VLE data. *Chem. Tech. (Leipzig)* **1998**, *50*, 17–19.

(8) Poethke, W. *Praktikum der Maßanalyse*; Harri Deutsch: Frankfurt (Main), Germany, 1987.

(9) Klauck, M.; Grenner, A.; Schmelzer, J. Liquid-liquid(-liquid) equilibria in ternary systems of water + cyclohexylamine + aromatic hydrocarbon (toluene or propylbenzene) or aliphatic hydrocarbon (heptane or octane). *J. Chem. Eng. Data* **2006**, *51*, 1034–1050.

(10) Klauck, M.; Grenner, A.; Taubert, K.; Martin, A.; Meinhardt, R.; Schmelzer, J. Vapor-liquid equilibria in binary systems of phenol or cresols + water, + toluene, + octane and liquid-liquid equilibria in

binary systems of cresols + water. *Ind. Eng. Chem. Res.* **2008**, *47*, 5119–5126.

(11) Schmelzer, J.; Taubert, K.; Martin, A.; Meinhardt, R.; Kempe, J. Phase equilibria in ternary systems containing phenols, hydrocarbons, and water. In *Thermodynamic Properties of Complex Fluid Mixtures*; Maurer, G., Ed.; Wiley-VCH: Weinheim, Germany, 2004; pp 135−149.

(12) Elliott, J. R.; Lira, C. T. http://www.egr.msu.edu/∼lira/readcomp.htm (esdparms.txt from progpack.exe; accessed December 2005).