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Isobaric Low-Pressure Vapor−Liquid Equilibrium Data for Ethylbenzene + Styrene + Sulfolane and the Three Constituent Binary Systems

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ABSTRACT: Isobaric vapor−liquid equilibrium (VLE) data have been measured for the ternary system (ethylbenzene + styrene + sulfolane) and the three constituent binary systems under vacuum [(5, 10, and 20) kPa]. The VLE data of the binary system (ethylbenzene + styrene) measured in this work are thermodynamically consistent according to the Herington area test and the point test method contrary to the low pressure VLE data about this system available in the literature. The binary VLE data were described well by the nonrandom two-liquid (NRTL) model. The relative volatility of the system (ethylbenzene + styrene) increases in the presence of sulfolane from 1.4 up to values of 2.2. The ternary system could only be well-correlated when using the ternary VLE data in combination with the binary VLE data as input for the regression of the NRTL binary interaction parameters.

INTRODUCTION

Styrene is mainly produced via the dehydrogenation of ethylbenzene.[1] The unreacted ethylbenzene and styrene are separated by a vacuum distillation column operating at (5 to 20) kPa.[2] Due to their close boiling points,[3] this distillation column accounts for (75 to 80) % of the total energy requirement in the separation section.[2] Extractive distillation is a promising alternative to reduce the energy requirements to separate ethylbenzene from styrene.[3,4] In extractive distillation a solvent is fed to a distillation column, which modifies the activity coefficients of the components to be separated and thereby enhances the relative volatility.[5] The relative volatility is defined as

$$\alpha = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i P_i^o}{\gamma_j P_j^o} \tag{1}$$

where y and x are the mole fractions of the components in the vapor and liquid phase, respectively, γ is the activity coefficient, P^o is the vapor pressure, and the subscripts correspond to components i and j. Sulfolane is a promising solvent, which can increase the relative volatility from 1.3 to 1.4 up to 2.4.[3] Sulfolane is a common solvent in extraction and extractive distillation processes.[3,6−8] Nevertheless, no process evaluation is available in the open literature for the ethylbenzene/styrene separation by extractive distillation using sulfolane. Consistent vapor−liquid equilibrium (VLE) data are mandatory to establish an equilibrium process model to investigate the potential to separate the mixture ethylbenzene/styrene by extractive distillation using sulfolane.[9] This requires VLE data for the three binary systems (ethylbenzene + styrene), (ethylbenzene + sulfolane), and (styrene + sulfolane), as well as the ternary system (ethylbenzene + styrene + sulfolane). In this work an overview is given of the relevant VLE data available in the literature of this system followed by the results of the VLE data measured in our laboratory. This is an expanded version of a previously published report of our work.[10] Specifically, we have previously reported the binary VLE data for (ethylbenzene + styrene) at (5, 10, and 20) kPa, the binary VLE data for (ethylbenzene + sulfolane) and (styrene + sulfolane) at (10 and 20) kPa, and some preliminary results of the relative volatilities for the ternary system at (5, 10, and 20) kPa for a solvent to feed (S/F) ratio of 2.5 on mass base to show that sulfolane indeed enhances the relative volatility. In that previous publication, we modeled the binary VLE data with the NRTL and Wilson equations using the modified Barker's method as the objective function. Because it was not possible to describe the ternary VLE data properly from the three binaries, we report here ternary VLE data at four different S/F ratios and refit the NRTL parameters using both binary and ternary VLE data and the ordinary least-squares objective function. Moreover, we add the 50 mbar data for the (ethylbenzene + sulfolane) and (styrene + sulfolane) binaries, show the relative volatilities for the (ethylbenzene + styrene) binary, and demonstrate the thermodynamic consistency of the data. In addition, we make the data available in tabular form for easy use by other researchers.

Prior to our previous publication,[10] no ternary data for these systems are reported in the literature. Data for the binary system (ethylbenzene + styrene) isobaric[11−16] as well as isothermic[17−19] data are presented in the literature. An overview of the relevant low pressure data of the binary system (ethylbenzene + styrene) and the binary systems (ethylbenzene + sulfolane) and (styrene + sulfolane) is presented in Table 1. For the binary system (ethylbenzene + styrene) only the data determined by Aucejo et al.,[11] Chaiyavech and van Winkle,[12] and White and van Winkle[13] are presented in Table 1. The other available data are thermodynamically inconsistent according to the point test method[20] which was reported by Aucejo et al.[11] The experimental data are consistent according to the point test method provided that the absolute average deviation between the

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Table 1. Overview of Reported Binary Vapor−Liquid Equilibrium Data for the System (Ethylbenzene + Styrene + Sulfolane)[10]

source	isobaric/isothermal	pressure/kPa	area consistency/%	AAD_{y_1}[a]
		Ethylbenzene (1) + Styrene (2)		
Aucejo et al.[11]	isobaric	5	68.1	0.003
	isobaric	15	21.3	0.001
Chaiyavech and van Winkle[12]	isobaric	6.7	55.0	0.005
	isobaric	13.3	51.7	0.004
	isobaric	26.7	93.2	0.008
White and van Winkle[13]	isobaric	13.3	51.9	0.01
		Ethylbenzene (1) + Sulfolane (2)		
Yu et al.[24]	isobaric	101.3		0.002
		Styrene (1) + Sulfolane (2)		
Chen and Zheng[37]	isothermal	0.04−5		

[a] Average absolute deviation in vapor mole fraction: $\mathrm{AAD}_{y_1} = (1/N)\Sigma_{i=1}^{N}|y_1^{\mathrm{exp}} - y_1^{\mathrm{cal}}|$($N$, number of data points).

Table 2. Experimental Pure Component Vapor Pressure Data

ethylbenzene		styrene	
T/K	P/kPa	T/K	P/kPa
324.4	5.00	332.4	5.00
333.4	7.50	341.4	7.50
340.0	10.00	348.3	10.00
345.5	12.50	353.9	12.50
350.1	15.00	358.5	15.00
354.1	17.50	362.6	17.50
357.7	20.00	366.2	20.00
360.9	22.50	369.4	22.50
363.8	25.00	372.4	25.00

Table 3. Antoine Parameters of the Pure Components in eq 2

component	T/K	A_i	B_i/K	C_i/K	AAD_P[a]/Pa
ethylbenzene[b]	324−364	20.8051	3211.78	−63.05	4.5
styrene[b]	332−373	21.1275	3453.58	−58.50	8.2
sulfolane[c]	391.2−558.2	21.9503	5193.41	−61.76	-

[a] Average absolute deviation in vapor pressure: $\mathrm{AAD}_P = (1/N)\Sigma_i^N|P_i^{\mathrm{exp}} - p_i^{\mathrm{cal}}|$ (N, number of data points). [b] Antoine parameters for ethylbenzene and styrene were determined from experimental data.[10] [c] Antoine parameters for sulfolane were taken from ref 25.

correlated and the experimental vapor mole fractions (AAD_y) is less than 0.01 and are scattered arbitrary around zero.[20] The area method developed by Redlich and Kister[21] and Herington[22] was applied to the available binary VLE data of the system (ethylbenzene + styrene) using the Aspen Plus Data Regression tool to determine the thermodynamic consistency. In the area method $\log(\gamma_1/\gamma_2)$ is plotted as function of the liquid mole fraction. The areas above and below the horizontal axis should be equal, where a maximum deviation of 10 % is allowed. Later, this method was extended by Herington to be able to apply it also to isobaric data,[23] since the influence of temperature on the activity coefficients was ignored in the original method.

From the Herington area consistency test, the conclusion can be drawn that the available low pressure (ethylbenzene + styrene) data are thermodynamically inconsistent. To determine the consistency of the VLE data, the experimental data of both the liquid and the vapor phase have to be known.[20,21] It was not possible to determine the consistency of the available (ethylbenzene + sulfolane) and (styrene + sulfolane) data, because the vapor phase compositions in these VLE data had to be calculated due to the large volatility difference between ethylbenzene/styrene and sulfolane.[24] The binary VLE data of the systems (ethylbenzene + sulfolane) and (styrene + sulfolane) were both not determined in the required pressure range of (5 to 20) kPa. To obtain a good calculation of the ternary VLE data from the binary VLE data sets, it is moreover recommendable to obtain all VLE data with the same experimental procedure in the same laboratory.[9] Thus, the three binaries and the ternary system were measured to obtain complete and consistent data in the required pressure range.

EXPERIMENTAL SECTION

Materials. Acetone (≥ 99.5 %) was obtained from VWR, cyclohexane (≥ 99 %) and styrene (≥ 99.5 %) from Merck, and ethylbenzene (≥ 99 %), sulfolane (≥ 98 %), and 4-*tert*-butylcatechol (≥ 98 %) from Fluka. All chemicals were used without further purification.

Apparatus and Procedure. All experimental VLE data were measured with an all-glass ebulliometer (Fischer VLE 602D), which is described in our previously published work.[10] The pressure of this apparatus could be determined with an accuracy of 0.01 kPa. The equilibrium temperature was measured with an accuracy of ± 0.1 K. Isobaric VLE data for the binary systems (ethylbenzene + styrene), (ethylbenzene + sulfolane), and (styrene + sulfolane) as well as the ternary system (ethylbenzene + styrene + sulfolane) were determined at (5, 10, and 20) kPa. The VLE data for the ternary system was determined at 4 mass based S/F ratios; 1, 2, 3, and 4, and three ethylbenzene/styrene mass ratios; 20:80, 50:50, and 80:20. 4-*tert*-Butylcatechol (0.005 wt %) was added as an inhibitor to prevent polymerization to the mixtures containing styrene. To determine the equilibrium compositions, samples of 20 μL were taken from the liquid and condensed vapor phases with a 100 μL syringe. Samples of 120 μL of acetone and 10 μL of cyclohexane were added respectively as a diluent and internal standard. The compositions were determined with a gas chromatograph (Varian CP-3800) equipped with a flame ionization detector and a Varian CP-SIL 5CB column (25 m × 1.2 μm). The split ratio of the gas

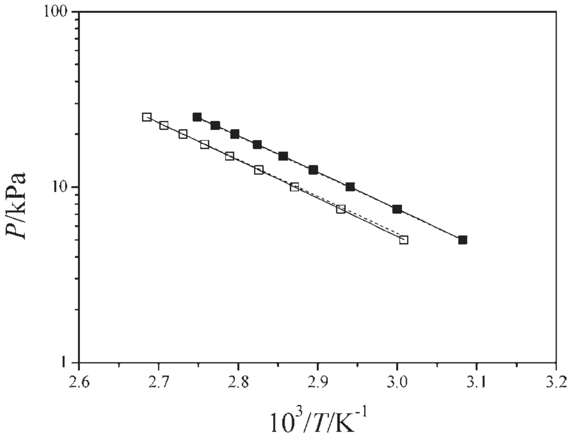


Figure 1. Pure component vapor pressures: ■, ethylbenzene;[10] □, styrene;[10] solid lines, Antoine correlations with parameters from Table 3; dashed lines, Antoine correlations from ref 25.

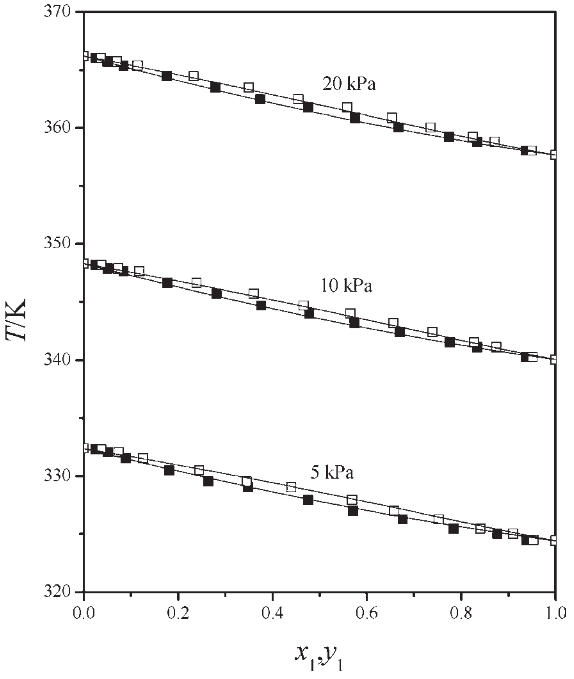


Figure 2. VLE temperature T against the liquid phase mole fraction x_1 and vapor phase mole fraction y_1 for the binary system ethylbenzene (1) + styrene (2) at (5, 10, and 20) kPa.[10] ■, □, experimental data; solid lines, NRTL.

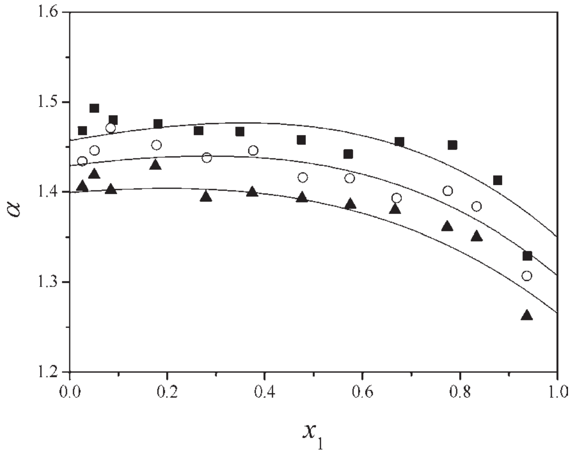


Figure 3. Relative volatility α as function of the liquid mole fraction x_1 in the binary system ethylbenzene (1) + styrene (2). ■, 5 kPa; ○, 10 kPa; ▲, 20 kPa; solid lines, NRTL.

chromatograph was 50 and the injection volume 0.5 μL. The concentration of the components in the vapor and liquid phases could be determined with an average deviation in mole fraction of 0.002.

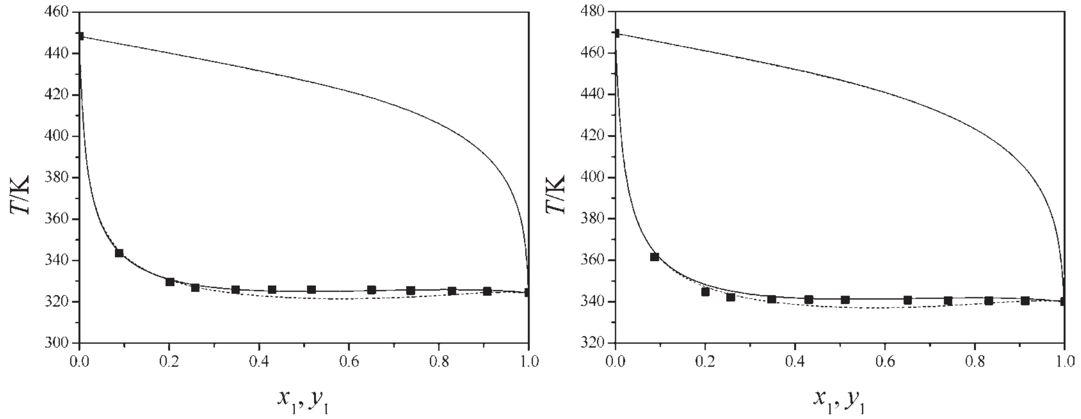
■ RESULTS AND DISCUSSION

Pure Component Vapor Pressures. The pure component vapor pressures of ethylbenzene and styrene were determined previously[10] in the relevant temperature range to validate the experimental method and are shown in Table 2. The Antoine equation was used to correlate the vapor pressures of ethylbenzene and styrene in ASPEN Plus, which is given in eq 2. The vapor pressure of sulfolane was calculated using parameters from the DECHEMA Chemistry Data Series by Gmehling and Onken.[25] The obtained Antoine parameters are presented in Table 3. The results for the pure component vapor pressures of ethylbenzene and styrene are depicted in Figure 1 together with the pure component vapor pressure data calculated with parameters from Gmehling and Onken.[25] It can be observed that the parameters from Gmehling and Onken give a fair correlation of the experimental data reported in this work for ethylbenzene (σP = 0.6 %) and styrene (σP = 1.2 %). From the absolute average deviation in pressure (see Table 3), the conclusion can be drawn that the Antoine equation can describe the experimental data very well.

$$\ln(P_i^\circ/\text{Pa}) = A_i - \frac{B_i}{(T/\text{K}) + C_i} \qquad (2)$$

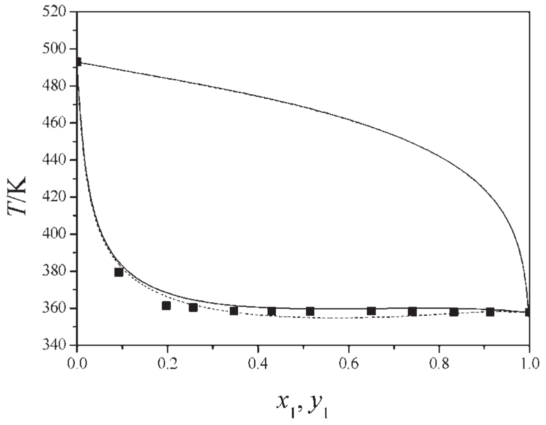
Binary VLE Data. The experimental temperature−composition diagram and the relative volatility α as function of the ethylbenzene liquid mole fraction x_{EB} of the binary system (ethylbenzene + styrene) are depicted in Figures 2[10] and 3, respectively. The experimental temperature−composition diagrams of the binary systems (ethylbenzene + sulfolane) and (styrene + sulfolane) are shown correspondingly in Figures 4 and 5,[10] where new data are shown for 5 kPa. The experimental values are listed in Tables 4 to 6. The system (ethylbenzene + styrene) forms an almost ideal mixture. The relative volatility of this mixture is increasing with decreasing pressure as is illustrated in Figure 3, which is a result of the increasing pure component vapor pressure ratio with decreasing temperature. It was determined that the experimental data are thermodynamically consistent according to the Herington area test method and the point test method. These tests were performed with the Aspen Plus Data Regression tool. The area deviations of the Herington method are (3.4, 1.1, and 0.4) % for correspondingly (5, 10, and 20) kPa. An example of this area test result is depicted in Figure 6 for 10 kPa.

The vapor concentration of sulfolane could not be determined with the gas chromatograph due to the big volatility difference between ethylbenzene/styrene and sulfolane.



a) 5 kPa

b) 10 kPa



c) 20 kPa

Figure 4. VLE temperature T against the liquid phase mole fraction x_1 and vapor phase mole fraction y_1 for the binary system ethylbenzene (1) + sulfolane (2) at (5, 10,[10] and 20[10]) kPa. ■, experimental data; solid lines, NRTL correlations with parameters determined solely from binary VLE data; dashed lines, NRTL correlations with parameters determined from a combination of binary and ternary VLE data.

However to regress the VLE data, the sulfolane vapor concentration is required. Raoult's law was applied to obtain an initial value for the sulfolane vapor concentration. The binary VLE data were previously[10] correlated in ASPEN Plus with the NRTL[26] and Wilson[27] activity coefficient models. The NRTL model is able to correlate from binary interaction parameters binary as well as ternary VLE data.[28] The Wilson model is also able to do this; however, the Wilson model was not able to describe the ternary VLE data reported in this work adequately. The required binary interaction parameters for the NRTL model are given by eq 3.

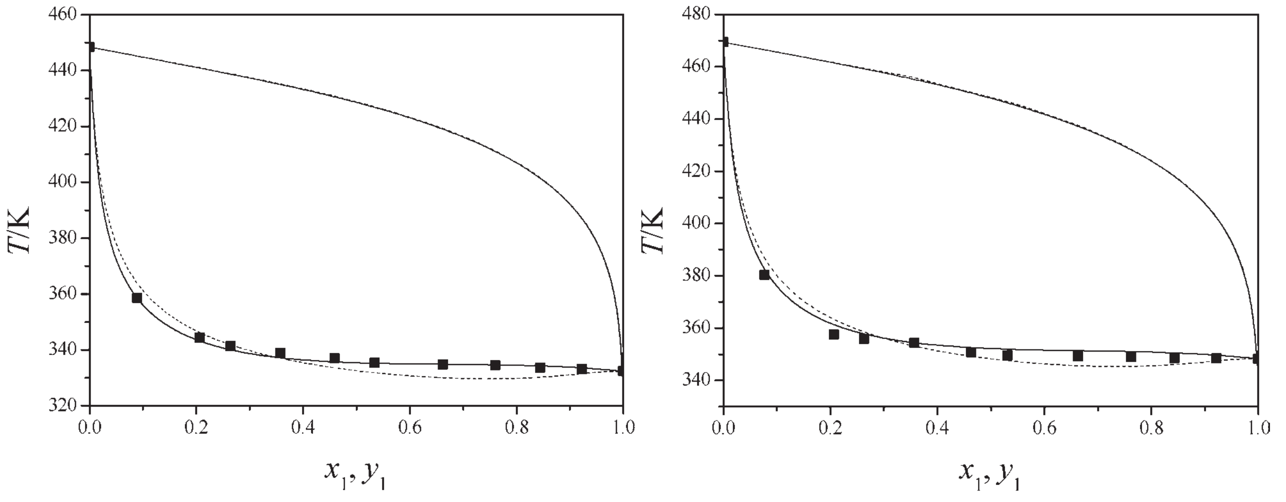
$$\tau_{ij} = \frac{A_{ij}}{RT}, \qquad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}),$$
$$\alpha_{ij} = \alpha_{ji} \quad \text{for} \quad i \neq j \quad \text{where} \quad i, j = 1, 2 \tag{3}$$

A_{ij} is a parameter characterizing the interaction energy between the molecules i and j and is acquired by regression of the experimental VLE data. The nonrandomness parameter α_{ij} was kept constant at 0.3, which is ordinary for nonpolar systems.[26] The vapor phase was considered as ideal, since the experimental pressures were well below atmospheric pressure.[28] The ordinary least-squares method was used as objective function (OF) and is defined as

$$\mathrm{OF} = \sum_{n=1}^{\mathrm{NDG}} w_n \sum_{i=1}^{N} \left[\left(\frac{T_i^{\mathrm{exp}} - T_i^{\mathrm{cal}}}{\sigma_T} \right)^2 + \left(\frac{y_i^{\mathrm{exp}} - y_i^{\mathrm{cal}}}{\sigma_y} \right)^2 \right] \tag{4}$$

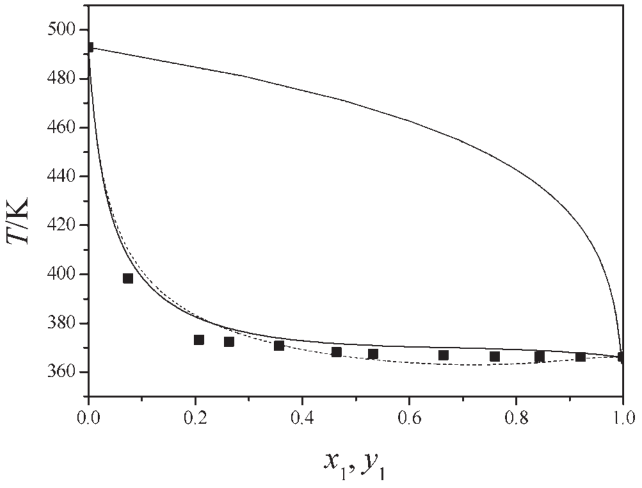
where NDG is the number of data groups, w_n is the weight of data group n, N is the number of data points, i is the data for data point i, and σ is the standard deviation of the indicated data. The binary interaction parameters and correlation statistics obtained from the regression of the experimental data are correspondingly summarized in Tables 7 and 8. By inspection of Figures 2 to 5 and the correlation statistics presented in Table 8, the conclusion can be drawn that the NRTL model adequately describes the binary experimental data.

Ternary VLE Data. The effect of the solvent-to-feed ratio on the relative volatility α is shown in Figure 7 for an ethylbenzene/styrene mass ratio of 50:50. The results for the ethylbenzene/styrene ratios 20:80 and 80:20 are comparable and are listed in Table 9. It can be seen from Figure 7 that sulfolane largely increases the relative volatility of the (ethylbenzene + styrene) system. The relative volatility is increasing with increasing solvent to feed ratio and



a) 5 kPa

b) 10 kPa



c) 20 kPa

Figure 5. VLE temperature T against the liquid phase mole fraction x_1 and vapor phase mole fraction y_1 for the binary system styrene (1) + sulfolane (2) at (5, 10,[10] and 20[10]) kPa. ■, experimental data; solid lines, NRTL correlations with parameters determined solely from binary VLE data; dashed lines, NRTL correlations with parameters determined from a combination of binary and ternary VLE data.

decreasing pressure. The increase of the relative volatility with an increasing solvent-to-feed ratio is a common behavior of ternary systems in extractive distillation units.[5,29,30] The increasing relative volatility with decreasing pressure can be explained by the higher pure component vapor pressure ratio at lower temperatures, similar to the binary system (ethylbenzene + styrene). Moreover the ratio of activity coefficients increases slightly with decreasing pressure. With the binary NRTL interaction parameters determined for the three constituent binary systems, a calculation was made for the relative volatility to investigate if the ternary system could be calculated from the parameters determined solely for the binary systems. Although many ternary systems can be described by interaction parameters determined for the binary systems,[28,31−35] for the ternary system studied in this work it was not possible, as illustrated in Figure 7. The dashed lines in this figure do not fit well with the experimental values for the relative volatility. This can be explained by the change in thermodynamic behavior of the ternary system compared to the binary system, which is presented in Figure 8. In Figure 8 the activity coefficients of styrene γ_{SM} in the binary system (styrene + sulfolane) and the ternary system (ethylbenzene + styrene + sulfolane) are plotted. In the binary system (styrene + sulfolane) the activity coefficient of styrene increases with decreasing styrene mole fraction, which is a common behavior of binary systems.[24,28,36−38] In the ternary system, however, the activity coefficient of styrene slightly decreases with decreasing styrene mole fraction. Therefore, the experimental relative volatility is larger compared to the relative volatility calculated from the parameters solely determined from the binary systems. Therefore, a new regression was performed to determine improved interaction parameters that are able to describe the ternary as well as the binary VLE data. The binary interaction parameters determined for the binary system (ethylbenzene + styrene) were kept constant, and the parameters determined for the binary systems (ethylbenzene + sulfolane) and (styrene + sulfolane) were adjusted

Table 4. Experimental Vapor−Liquid Equilibrium Data for Ethylbenzene (1) + Styrene (2)

5 kPa			10 kPa			20 kPa		
T/K	x_1	y_1	T/K	x_1	y_1	T/K	x_1	y_1
332.3	0.026	0.037	348.2	0.026	0.037	366.0	0.026	0.036
332.1	0.051	0.074	347.9	0.051	0.073	365.7	0.05	0.070
331.5	0.089	0.126	347.6	0.084	0.118	365.4	0.084	0.114
330.5	0.181	0.245	346.6	0.178	0.239	364.5	0.176	0.233
329.5	0.264	0.346	345.7	0.281	0.360	363.5	0.279	0.350
329.1	0.349	0.440	344.7	0.376	0.466	362.5	0.374	0.455
327.9	0.475	0.569	344.0	0.478	0.565	361.8	0.476	0.558
327.0	0.571	0.658	343.2	0.574	0.656	360.9	0.575	0.653
326.3	0.676	0.752	342.4	0.670	0.739	360.0	0.667	0.735
325.5	0.784	0.841	341.5	0.775	0.828	359.2	0.774	0.824
325.0	0.877	0.910	341.1	0.834	0.874	358.8	0.834	0.871
324.5	0.938	0.953	340.3	0.937	0.951	358.0	0.937	0.949

Table 5. Experimental Vapor−Liquid Equilibrium Data for Ethylbenzene (1) + Sulfolane (2)

5 kPa		10 kPa		20 kPa	
T/K	x_1	T/K	x_1	T/K	x_1
343.6	0.089	361.5	0.088	379.4	0.092
329.6	0.202	344.8	0.201	361.4	0.197
326.9	0.258	342.2	0.257	360.3	0.257
325.9	0.348	341.1	0.348	358.4	0.347
325.9	0.429	341.0	0.431	358.4	0.430
325.9	0.517	340.8	0.512	358.3	0.515
325.8	0.650	340.7	0.651	358.4	0.650
325.5	0.737	340.6	0.740	358.2	0.741
325.3	0.829	340.5	0.831	357.9	0.833
325.0	0.908	340.4	0.912	357.8	0.913

Table 6. Experimental Vapor−Liquid Equilibrium Data for Styrene (1) + Sulfolane (2)

5 kPa		10 kPa		20 kPa	
T/K	x_1	T/K	x_1	T/K	x_1
358.6	0.089	380.3	0.077	398.4	0.075
344.3	0.207	357.5	0.207	373.2	0.207
341.4	0.264	355.9	0.263	372.5	0.263
338.9	0.358	354.3	0.357	370.7	0.357
337.1	0.459	350.8	0.463	368.2	0.464
335.4	0.534	349.6	0.531	367.4	0.532
334.8	0.662	349.1	0.663	366.9	0.664
334.4	0.760	348.9	0.762	366.4	0.760
333.7	0.844	348.6	0.843	366.3	0.843
333.2	0.923	348.4	0.922	366.2	0.920

during the regression of the ternary VLE data. The binary and ternary VLE data were both used as input for the regression. Weight factors of 10 and 1 were given respectively to the ternary and binary VLE data. The weight factor of 10 dedicated to the ternary data was

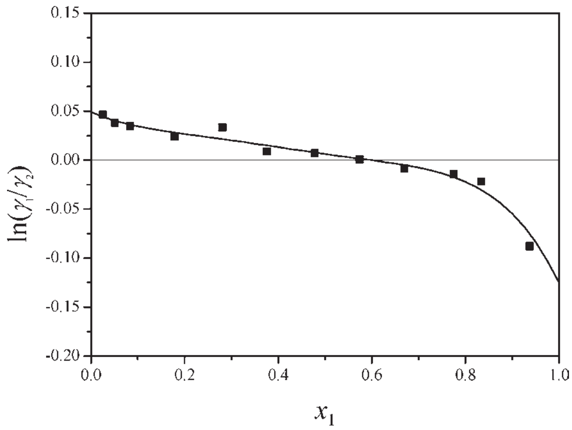


Figure 6. Thermodynamic consistency test for the binary system ethylbenzene (1) + styrene (2) at 10 kPa. ■, experimental data; solid line, experimental data fit.

Table 7. NRTL Binary Interaction Parameters for the Three Binary Systems Determined from the Binary VLE Data and Combination of Binary + Ternary VLE Data

system	A_{12} / J·mol^{-1}	A_{21} / J·mol^{-1}	α_{12}
	From Solely Binary VLE Data		
ethylbenzene (1) + styrene (2)	2532.5	−1884.9	0.3 (fixed)
ethylbenzene (1) + sulfolane (2)	6473.0	1821.3	0.3 (fixed)
styrene (1) + sulfolane (2)	5435.3	1310.0	0.3 (fixed)
	From Binary + Ternary VLE Data		
ethylbenzene (1) + sulfolane (2)	11393.5	1677.1	0.321
styrene (1) + sulfolane (2)	15713.9	1055.5	0.352

Table 8. Absolute Average Deviations in Vapor Mole Fraction, Pressure, and Relative Volatility for the Calculation of the VLE Data by the NRTL Model

system	AAD$_{y_1}$[a]	AAD$_T$[b]/K	AAD$_\alpha$[c]
	From Solely Binary VLE Data		
ethylbenzene (1) + styrene (2)	0.0011	0.1	0.015
ethylbenzene (1) + sulfolane (2)	0.0011	1.5	
styrene (1) + sulfolane (2)	0.0020	2.0	
	From Binary + Ternary VLE Data		
ethylbenzene (1) + sulfolane (2)	0.0001	1.8	
styrene (1) + sulfolane (2)	0.0020	2.8	
ethylbenzene (1) + styrene (2) + sulfolane (3)	0.0044	2.4	0.043

[a] Average absolute deviation in vapor mole fraction: $\mathrm{AAD}_{y_1} = (1/N)\Sigma_i^N|y_1^{\mathrm{exp}} - y_1^{\mathrm{cal}}|$($N$, number of data points). [b] Average absolute deviation in pressure: $\mathrm{AAD}_P = (1/N)\Sigma_i^N|P^{\mathrm{exp}} - P^{\mathrm{cal}}|$. [c] Average absolute deviation in relative volatility of the ternary VLE data: $\mathrm{AAD}_\alpha = (1/N)\Sigma_i^N|\alpha^{\mathrm{exp}} - \alpha^{\mathrm{cal}}|$.

Table 9. Experimental Vapor–Liquid Equilibrium Data for the Ternary System Ethylbenzene (1) + Styrene (2) + Sulfolane (3) at (5, 10, and 20) kPa

T/K	x_1	x_2	y_1	y_2
5 kPa				
326.9	0.413	0.107	0.880	0.119
328.0	0.276	0.074	0.887	0.112
328.8	0.204	0.056	0.893	0.106
329.5	0.253	0.273	0.643	0.356
331.2	0.167	0.187	0.652	0.346
332.2	0.119	0.406	0.361	0.638
332.6	0.157	0.045	0.886	0.112
333.1	0.121	0.137	0.657	0.341
335.2	0.077	0.274	0.367	0.631
337.4	0.059	0.203	0.378	0.619
337.4	0.094	0.110	0.659	0.338
341.9	0.042	0.163	0.364	0.632
10 kPa				
342.7	0.415	0.108	0.873	0.125
343.2	0.276	0.074	0.883	0.115
344.2	0.202	0.055	0.888	0.110
345.1	0.254	0.269	0.630	0.369
346.8	0.164	0.185	0.644	0.354
347.3	0.157	0.047	0.880	0.117
347.4	0.120	0.405	0.352	0.646
348.6	0.122	0.137	0.646	0.351
350.5	0.077	0.273	0.360	0.637
350.9	0.094	0.111	0.647	0.349
352.5	0.059	0.203	0.368	0.628
355.0	0.042	0.164	0.353	0.641
20 kPa				
360.0	0.414	0.106	0.867	0.131
360.4	0.276	0.073	0.874	0.122
362.5	0.251	0.275	0.617	0.380
362.7	0.202	0.056	0.878	0.118
363.2	0.157	0.045	0.870	0.125
363.3	0.164	0.185	0.627	0.369
364.8	0.118	0.403	0.339	0.658
366.4	0.121	0.138	0.628	0.367
366.7	0.096	0.109	0.633	0.361
366.9	0.076	0.271	0.346	0.649
369.2	0.058	0.201	0.351	0.644
369.8	0.042	0.160	0.342	0.652

essential to get a proper correlation for the relative volatility of the ternary system. Furthermore, it was required to regress also the nonrandomness parameter to get a proper correlation for the ternary VLE data. The improved binary interaction parameters determined for the combination of the binary and ternary VLE data are given in Table 7. From Figure 7, the conclusion can be drawn that the improved binary interaction parameters provide a much better description of the ternary VLE data. Nevertheless, the binary VLE data of the systems (ethylbenzene + sulfolane) and (styrene + sulfolane) are described less accurately if the binary and ternary VLE data are regressed together. This conclusion can be drawn from the temperature–composition diagrams depicted in Figures 4 and 5 and from the correlation statistics shown in Table 8.

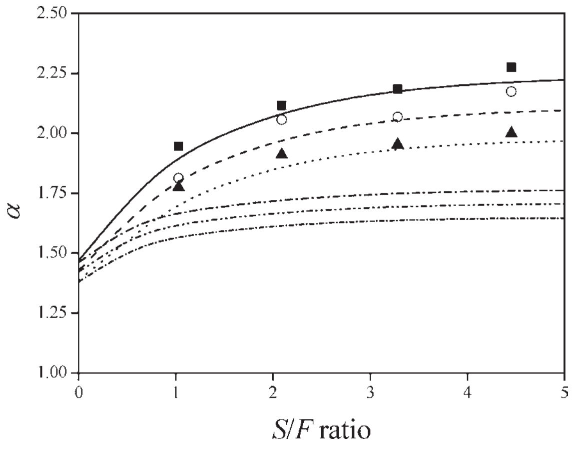


Figure 7. Relative volatility α of the ethylbenzene (1) + styrene (2) system in the presence of sulfolane as function of the molar solvent-to-feed (*S*/*F*) ratio. ■, 5 kPa; ○, 10 kPa; ▲, 20 kPa; experimental data. —, 5 kPa; — —, 10 kPa; · · ·, 20 kPa; relative volatility calculated with NRTL parameters determined from a combination of binary and ternary VLE data. ·—·, 5 kPa; ··—··, 10 kPa; ·—·, 20 kPa; relative volatility calculated with NRTL parameters determined solely from the three binary systems.

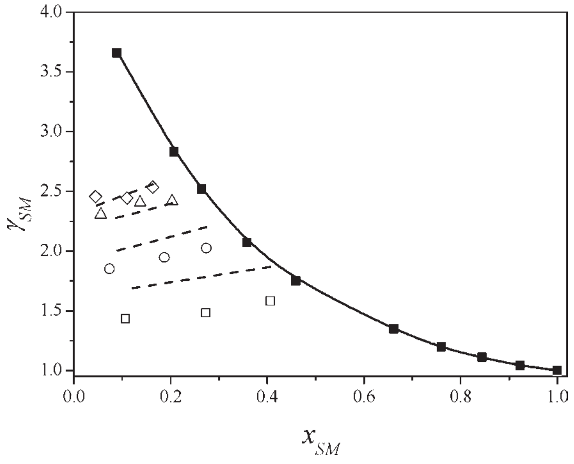


Figure 8. Activity coefficient of styrene γ_{SM} in the binary system (styrene + sulfolane) as well as the ternary system (ethylbenzene + styrene + sulfolane) as a function of the styrene liquid mole fraction x_{SM} at 5 kPa. ■, activity coefficient of styrene γ_{SM} in the binary system (styrene + sulfolane); □, *S*/*F* = 1; ○, *S*/*F* = 2; △, *S*/*F* = 3; ◊, *S*/*F* = 4; γ_{SM} in the ternary system (styrene + ethylbenzene + sulfolane); —, NRTL correlations for the binary VLE data; — —, NRTL correlations with parameters determined from a combination of binary and ternary VLE data.

■ CONCLUSIONS

In this work, we expand upon our previously published[10] isobaric binary and ternary VLE data, which were determined for the system (ethylbenzene + styrene + sulfolane) under vacuum

[(5, 10, and 20) kPa]. The measured binary VLE data of the system (ethylbenzene + styrene) is thermodynamically consistent in contrast to the available data in literature. All binary experimental VLE data could be well-correlated by the NRTL model. It was not possible to adequately correlate the experimental ternary VLE data with the binary interaction parameters determined for the binary systems, since the activity coefficient of styrene slightly decreases with decreasing mole fraction in the ternary system, unlike in the binary system. The ternary system (ethylbenzene + styrene + sulfolane) can only be described well if the ternary data are also included in the regression of the binary interaction parameters.

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