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Vapor–Liquid Equilibrium for the Mixture of m-Xylene, Ethylbenzene and 1, 2, 4-Trichlorobenzene at 101.3 kPa

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Abstract

The vapor-liquid phase equilibrium (VLE) data for binary systems of m-xylene + ethylbenzene, m-xylene + 1, 2, 4-trichlorobenzene, ethylbenzene + 1, 2, 4-trichlorobenzene and ternary system of m-xylene + ethylbenzene + 1, 2, 4-trichlorobenzene were determined with a modified Rose still at 101.3 kPa, and all the binary data passed the Wisniak's test, which accorded with the thermodynamic consistency. Three activity coefficient models namely, Wilson, NRTL and UNIQUAC were used to correlate VLE data and get binary interaction parameters, then the ternary VLE data of m-xylene + ethylbenzene + 1, 2, 4-trichlorobenzene were estimated based on these model parameters using Aspen Plus software. The estimation values of the three models agree well with the experimental data. Moreover, the effect of 1, 2, 4-trichlorobenzene was analyzed, and it found to be an effective candidate extractant for the extractive distillation of ethylbenzene from mixed xylenes.

Key words: m-Xylene, Ethylbenzene, 1, 2, 4-Trichlorobenzene, VLE, Thermodynamics model

1. Introduction

Ethylbenzene and xylenes are C₈ benzene homologues, called “mixed xylenes”¹, containing o-xylene, m-xylene, p-xylene, and ethylbenzene, which are mainly derived from catalytic reforming of petroleum fractions, cracking gasoline and crude benzene by coking. Mixed xylenes are of great importance in petrochemical industry¹⁻², since they are the main raw materials for the synthesis of many organic compounds²⁻⁸. Recently, the demand for every one of these compounds has grown very rapidly⁷. For example, m-xylene is a raw material for the synthesis of isophthalic acid used in polyesters,³⁻⁴ p-xylene could be converted to terephthalic acid, then terephthalic acid and ethanediol react to produce polyester.⁷ Ethylbenzene is mainly used for the synthesis of styrene.⁸

In general, with an industrially isomerization process⁹, ethylbenzene and xylenes could be converted into the mixture containing only xylenes, namely o-, m-, p-xylene (mainly p-xylene). However, the isomerization process causes the loss of xylenes unavoidably, and dealkylation also occurs in which, then undesired benzene, toluene and alkane will be acquired as byproducts. Furthermore, high ethylbenzene residue of end-product results in low added value of xylenes products. It is a diluent which can accumulate in recycle process and, hence, has a strong affect on the separation of the individual xylene isomers. Accordingly, the ethylbenzene separation from mixed xylenes should be taken into account, since the removal of ethylbenzene simplifies the subsequent separation of the xylenes.

However, the production of pure ethylbenzene or individual xylene isomers by

common distillation is technically difficult as a result of the similar boiling points of these compounds.¹⁰ For example, ethylbenzene could be separated from the remaining isomers via a distillation tower with more than 300 trays. Thus, extraction distillation¹⁰⁻¹¹ can be used in the separation of C8 aromatic isomers. As extractants¹², several solvents have been demonstrated effective to this distillation process, such as phthalic anhydride, maleic anhydride and the mixture of first two,¹³ chlorinated organic compounds¹⁴. Then, 1, 2, 4-trichlorobenzene (hereinafter referred to as trichlorobenzene) was chosen the target extractive solvent in order to enhance the relative volatility of ethylbenzene and xylenes. Therefore, for systems containing ethylbenzene, xylenes and trichlorobenzene, accurate vapor liquid equilibrium (VLE) data are essential for the simulation and design of the distillation process. In this article, the VLE phenomenon for the mixture of m-xylene + ethylbenzene + trichlorobenzene was discussed. For what we can tell, there have no VLE data to be found for binary systems of trichlorobenzene + ethylbenzene, or trichlorobenzene + m-xylene in literature. Up to now, only the VLE data for the binary system of m-xylene + ethylbenzene have been published.¹⁵⁻¹⁷

In this work, the isobaric VLE data for three binary systems and a ternary system are reported namely, m-xylene + ethylbenzene, m-xylene + trichlorobenzene, ethylbenzene + trichlorobenzene and m-xylene + ethylbenzene + trichlorobenzene, at 101.3 kPa. The experimental data for these binary systems all passed L-W test of Wisniak's¹⁸⁻¹⁹, indicating that they are thermodynamically consistent. The Wilson²⁰, nonrandom two-liquid (NRTL)²¹, and universal quasichemical activity coefficient

(UNIQUAC)²² models were used to correlate the experimental data of each binary mixture to obtain their correlation parameters, then these model parameters fitted by binary VLE data were employed to predict ternary VLE data of m-xylene + ethylbenzene + trichlorobenzene. Meanwhile, the experimental binary and ternary VLE data were compared with the predicted values. The experimental results agree well with predicted. These experimental data could be the foundation to design the extraction distillation process for the ethylbenzene separation from the mixed xylenes.

2. Experimental section

2.1 Materials

The specific information of the reagents used in the experiment are shown in Table 1. All these chemicals were high-purity level and without further purification, checking with gas chromatograph (GC, GC7890A, Agilent, USA), and no obvious impurity peaks were detected.

2.2 Sample Analysis

Gas chromatograph (GC), equipped with a flame ionization detector (FID) and a polyethylene glycol packed column (PEG-20M, 60 m × 0.32 mm × 0.33 μm), was used for sample analysis. Isopropanol was the internal standard. The carrier gas was high-purity nitrogen with flow rate of 25 mL/min, and the hydrogen and air flow rate were 30 mL/min and 300 mL/min, respectively. The column inlet pressure was 0.1 MPa, and the split ratio was 50. The injector temperature and detector temperature were both 200 °C, and the sample injection volume was 0.2 μL. The programmed temperature of GC was set within the temperature range of 110~230 °C. The initial

temperature was 110 °C and kept for 5 minutes, then rose to 230 °C with 20 °C/min and maintained for 3 min. Quantitative analysis was carried out by the area correction method. To ensure the accuracy of the analysis, each sample was measured at least three times, and the average value of the three data within 0.1% of the error was taken as the final experimental record. For the same purpose, all vapor-liquid equilibrium data were generated with temperature and pressure stable for 1.5 h or longer.

2.3 Apparatus and procedure

As shown in Figure 1, a modified Rose vapor-liquid equilibrium still was used to determine the VLE data. The energy of the whole system was provided by a resistance wire heating device in the still, and the heating was controlled by adjusting the voltage. At the beginning, the voltage of the transformer was slowly adjusted to make the liquid boil. A magnet was added in the boiling chamber, and the rotating speed was adjusted by a magnetic stirrer, so that the mixture could be mixed evenly and the violent boiling could be effectively suppressed. The stagnation zone was adjusted by the cocks on both sides of the device to reduce dead angles in the circulation circuit. The low temperature thermostat continuously provides -10 °C of reflux liquid to ensure that the vapor phase was fully condensed, then more accurate analysis for vapor phase composition could be obtained. When the liquid in the equilibrium cell reached a stable circulation, we believed that it had reached the vapor-liquid equilibrium state and kept the voltage unchanged at this time.

A precision thermometer, corrected by freezing point and dew neck, was used to measure the temperature with an accuracy of 0.05 °C. During the experiment, the

mercury column was completely immersed in dimethyl silicone oil, and the outside of the device was wrapped with thermal insulation cotton to prevent heat loss. The pressure of the VLE system was set using the ZKY-2000C-80H digital vacuum measurement with an error of less than 0.025 kPa, and the system pressure was controlled at 101.3 ± 0.03 kPa, which was implemented by using suction system. The atmospheric pressure in the laboratory was determined by the DYM3 empty box barometer.

2.4 Verification of the device reliability

Moreover, in order to ensure the accuracy of the experimental results, the reliability of the device and the experimental method was validated. The data for known binary system namely, water + acetic acid were generated at 101.3 kPa. The experimental data of vapor-liquid phase equilibrium measured by this device under 101.3 kPa were compared with the literature data²³⁻²⁵, and the deviation between the two was observed (Figure 2). The experimental and the literature data matched well, thus verifying the reliability of the device and the accuracy of the experimental method.

3. Results and discussion

3.1. VLE Model.

The γ - Φ approach employs an activity coefficient model to determine the liquid-phase nonidealities and an equation of state to determine the fugacity coefficient, which accounts for the nonidealities in the vapor phase. The γ - Φ formulation²⁶ for VLE at low and moderate pressures is represented as follows:

$$y_i \phi_i p = x_i \gamma_i p_i^s \quad (1)$$

Where y_i and x_i are the vapor-phase and liquid-phase mole fraction of component i , respectively, $\phi_i = \phi_i^v / \phi_i^s \exp\left[-\frac{v_i^l(p - p_i^s)}{RT}\right]$, p is the total pressure of the system, γ_i represents the activity coefficient of component i , V_i^l represents the liquid phase molar volume of component i , and R is the molar gas constant. p_i^s represents the saturated vapor pressure of component i , calculated by the Antoine expansion equation Eq 2. The various parameters in the formula were acquired from the Aspen Plus V10 physical property database, listed in Table 2.

$$\ln(p_i^s / \text{kPa}) = C_{1,i} + C_{2,i} / [T / K + C_{3,i}] + C_{4,i}(T / K) + C_{5,i} \ln(T / K) + C_{6,i}(T / K)^{C_{7,i}} \quad (2)$$

The vapor phase can be regarded as an ideal gas at low pressure, accordingly, ϕ_i in Eq 1 is approximately 1. Therefore, Eq 1 can be simplified to Eq 3.

$$y_i p = x_i \gamma_i p_i^s \quad (3)$$

3.2. VLE Data.

The isobaric VLE data of the binary systems of m-xylene + ethylbenzene, m-xylene + trichlorobenzene and ethylbenzene + trichlorobenzene determined at 101.3 kPa are listed in Tables 3, and the corresponding T - x - y phase diagram were plotted in Figures 3-5. The literature data of the system m-xylene + ethylbenzene were also listed in Figures 3. In this work, only the isobaric VLE literature data were compared with the experimental data. However, the literature data are determined at 100.65 kPa¹⁶, different from this work at 101.3 kPa. Accordingly it can be observed a little deviation between two sets of data in Figure 3, but these two curves have similar trends.

In addition, Table 7 and Figure 9 illustrate the experimental VLE data of the ternary system m-xylene + ethylbenzene + trichlorobenzene. In addition, the calculated activity coefficients γ_1 and γ_2 are listed in Table 3, confirming that the m-xylene + ethylbenzene system presents positive deviations; however, the m-xylene + trichlorobenzene and the ethylbenzene + trichlorobenzene systems display a negative deviation from Raoult's law.

3.3. Thermodynamic Consistency Tests of Binary Systems.

The Wisniak's L-W test¹⁸⁻¹⁹ was used to verify the thermodynamic consistency of the data obtained, which is based on the Gibbs–Duhem equation, can actualizes the point-to-point test and area test simultaneously. It can be described with the following equations:

$$D = 100 \times \frac{\left| \int_0^1 L_k dx_1 - \int_0^1 W_k dx_1 \right|}{\int_0^1 L_k dx_1 + \int_0^1 W_k dx_1} \quad (4)$$

$$L_k = \frac{\sum T_i^0 x_i \Delta s_i^0}{\sum x_i \Delta s_i^0} - T \quad (5)$$

$$W_k = \frac{RT}{\sum x_i \Delta s_i^0} \left(\sum x_i \ln \gamma_i - \sum x_i \ln \frac{y_i}{x_i} \right) \quad (6)$$

$$\Delta s_i^0 = \frac{\Delta h_i^0}{T_i^0} \quad (7)$$

Among them, T_i^0 is the boiling point of the pure component i at the equilibrium pressure, k represents each experimental point, Δs_i^0 is the enthalpy of vaporization of pure component i , and Δh_i^0 represents the enthalpy of vaporization of pure component i , which was taken from the Aspen Plus V10 physical properties databanks. The

deviation $D < 5$ in the Wisniak area test listed in Table 4 illustrates that the binary systems pass the area test. Additionally, as Figure 6 showed that all of the experimental points meet the $0.92 < L_k/W_k < 1.08$ criteria, which indicates that the VLE data pass the point-to-point test. These findings show that all the VLE data gained from the experiment are thermodynamically consistent.

3.4. Data Regression.

Under the regression environment in Aspen Plus V10, Wilson, NRTL and UNIQUAC thermodynamic models were used to fit VLE data of the binary systems. The maximum likelihood function²⁷⁻²⁸ was used for regression. The objective function (OF) is written as:

$$Q = \sum_{i=1}^N \left[\left(\frac{T_i^{\text{exp}} - T^{\text{est}}}{\sigma_T} \right)^2 + \left(\frac{p_i^{\text{exp}} - p_i^{\text{est}}}{\sigma_p} \right)^2 + \left(\frac{x_i^{\text{exp}} - x_i^{\text{est}}}{\sigma_x} \right)^2 + \left(\frac{y_i^{\text{exp}} - y_i^{\text{est}}}{\sigma_y} \right)^2 \right] \quad (8)$$

Where Q is the objective function, N is the number of experimental points, T is the equilibrium temperature, p is the equilibrium pressure, y and x are the composition of vapor and liquid phase, and the superscript *exp* and *est* are the experimental and estimated values, respectively. The binary interaction parameters obtained by regression were shown in Table 5. Fitted curves were plotted in Figures 3-5. In addition, root mean square deviation (RMSD)²⁹ and average absolute deviation (AAD)³⁰ in Eq 9 and Eq 10 were determined and the error were shown in Table 6.

$$\text{RMSD}(x_i) = \left(1/N \times \sum_{i=1}^N (x_i^{\text{exp}} - x_i^{\text{est}})^2 \right)^{1/2} \quad (9)$$

$$\text{AAD}(x_i) = 1/N \times \sum_{i=1}^N |x_i^{\text{exp}} - x_i^{\text{est}}| \quad (10)$$

The RMSD of T was no more than 0.25 K, and the AAD did not exceed 0.21 K; the RMSD of p was no more than 0.12 kPa, and the AAD did not exceed 0.08 kPa; the RMSD of y was no more than 0.0034, and the AAD did not exceed 0.0022. Therefore, Wilson, NRTL, and UNIQUAC models can all fit the experimental data well. Apparently, Wilson, NRTL, and UNIQUAC models can fit the experimental data well. The accuracy of the three models varies a little. Among them, for the system m-xylene + ethylbenzene and m-xylene + trichlorobenzene, the NRTL model performs better. As to the system ethylbenzene + trichlorobenzene, the UNIQUAC model fit the VLE data well.

However, charts like Figure 3 are unable to provide quantitative uncertainty estimates, particularly at the vicinity of the pure-component limits. As suggested by Mathias³¹⁻³², the qualities of the regressed data could be also evaluated by the calculated relative volatilities ($\alpha/-$), which can be defined by Eqs 11 and 12 as well as model K value errors (Eq 13) for both K_1 and K_2 . The relative volatility plots were plotted to evaluate the model uncertainty. As shown in Figure 7, the NRTL model uncertainty is 5% or better for three binary systems. In the case of model K -value errors (Figure 8), very low K_1 errors (<1%) can be represented over all x_1 concentration for three systems. The K_1 errors points increase with x_1 concentration in Figure 8 (a), while the other two sets of points distribute randomly in Figure 8 (b) and (c). Moreover, it can be observed that K_1 errors are higher below 0.6 x_1 concentration. The large errors could be the result of higher relative volatilities of the investigated mixtures. Anyhow, according to the analysis mentioned above, graphs described K_1

errors and relative volatilities show that Wilson activity coefficient equation is very suitable to be used to correlate binary VLE data for the system consisting of m-xylene, ethylbenzene and trichlorobenzene.

$$K_i = \frac{y_i}{x_i} \quad (11)$$

$$\alpha = \frac{K_1}{K_2} \quad (12)$$

$$K - \text{value error} = \frac{K_{\text{cal}} - K_{\text{exp}}}{K_{\text{exp}}} \quad (13)$$

3.5. Estimate of Ternary VLE Data.

The VLE of the m-xylene + ethylbenzene + trichlorobenzene ternary system was predicted based on the binary interaction parameters obtained by regression of the VLE data of the binary systems with three thermodynamic models. The comparison between the predicted and the experimental data was shown in Figure 9, and the calculated deviations were shown in Table 8.

As shown in the figure, the prediction results of the three models agree well with the experimental values. The average absolute deviation of T was no more than 1.0 K, and the average absolute deviation of y_i was no more than 0.05. In general, the calculation accuracy of the NRTL model was higher, and the Wilson and UNIQUAC models perform poorly. It also showed that the binary interaction parameters obtained through the binary system VLE experiment were reliable and could be used to predict the VLE data of the ternary system.

In the end, in order to find out the extractant effect on this system, the relative volatility of the ternary system of the m-xylene + ethylbenzene + trichlorobenzene

was calculated (Table 7). It is clear that added trichlorobenzene causes the enhancement of relative volatility. Accordingly, the distillation of m-xylene and ethylbenzene is also easier to implement. As well, the relative volatility is 1.17 when trichlorobenzene concentration is 0.85, highest over the whole range of concentration.

4. Conclusions

Vapor-liquid equilibrium data of the binary systems of m-xylene + ethylbenzene, m-xylene + trichlorobenzene, ethylbenzene + trichlorobenzene and the ternary system of m-xylene + ethylbenzene + trichlorobenzene were measured at 101.3 kPa. Experimental data for the mixtures of ethylbenzene with m-xylene and trichlorobenzene were correlated by Wilson, NRTL, and UNIQUAC activity coefficient models with Aspen Plus V10. The binary interaction parameters were used to predict the VLE data of the ternary system, and the NRTL model gave better prediction over the other two models. The calculated binary interaction parameters (BIPs) were found to be suitable to model vapor-liquid equilibrium of the mixture containing m-xylene + ethylbenzene + trichlorobenzene. Moreover, the results showed that the deviation between the estimated and the experimental values are within the allowable range. This work provides reliable VLE data for the design and scale-up of the distillation process. Obviously, added trichlorobenzene has positive effect on the distillation of m-xylene and ethylbenzene.

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Table 1. Physical data information for the chemical reagents at 101.3kPa^a

compound	CAS number	source	analysis method	mole fraction purity
m-xylene	108-38-3	Aladdin industrial corporation	GC ^b	≥0.995
ethylbenzene	100-41-4	Aladdin industrial corporation	GC ^b	≥0.995
trichlorobenzene	120-82-1	Aladdin industrial corporation	GC ^b	≥0.995
isopropanol	67-63-0	Sinopharm Chemical Reagent	GC ^b	≥0.998

^a Standard uncertainty u(P) = 0.03 kPa.

^b Gas chromatography.

Table 2. Antoine equation parameters of pure components^a

component	C1	C2	C3	C4	C5	C6	C7	T/°C
m-xylene	78.1912	-7615.9	0	0	-9.3072	5.56E-06	2	-47.85~343.85
ethylbenzene	82.1552	-7733.7	0	0	-9.917	5.99E-06	2	-94.95~344
trichlorobenzene	33.8932	-6659.1	0	0	-2.5549	4.69E-04	1	17~451.85

^a Taken from the Aspen Plus Pure Component Property Database.

Table 3. Isobaric VLE Data of Binary Systems m-xylene (1) + ethylbenzene (2), m-xylene (1) + trichlorobenzene (2), and ethylbenzene (1) + trichlorobenzene (2) at 101.3 kPa^a

<i>T</i> /K	<i>x</i> ₁	<i>y</i> ₁	<i>γ</i> ₁	<i>γ</i> ₂
m-xylene (1) + ethylbenzene (2)				
409.31	0.0000	0.0000	-	1.0000
409.57	0.1968	0.1910	1.0435	1.0002
409.61	0.2254	0.2188	1.0423	1.0005
409.65	0.2541	0.2466	1.0410	1.0009
409.8	0.3392	0.3290	1.0361	1.0022
409.86	0.3722	0.3609	1.0341	1.0031
409.94	0.4116	0.3990	1.0315	1.0044
410.1	0.4837	0.4686	1.0265	1.0076
410.18	0.5159	0.4998	1.0243	1.0094
410.25	0.5401	0.5233	1.0224	1.0108
410.38	0.5866	0.5686	1.0191	1.0143
410.51	0.6286	0.6096	1.0161	1.0179
410.85	0.7242	0.7044	1.0098	1.0286
410.94	0.7468	0.7272	1.0084	1.0317
411.1	0.7858	0.7669	1.0063	1.0376
411.48	0.8651	0.8498	1.0025	1.0513
411.7	0.9085	0.8966	1.0013	1.0604
412.24	1.0000	1.0000	1.0000	-
m-xylene (1) + trichlorobenzene (2)				
486.16	0.0000	0.0000	-	1.0000
462.57	0.1979	0.5573	0.8629	0.9882
457.04	0.2626	0.6548	0.8576	0.9701
450.07	0.3441	0.7534	0.8749	0.9419
438.34	0.4994	0.8790	0.9168	0.8456
432.22	0.5886	0.9230	0.9440	0.7857
428.21	0.6525	0.9455	0.9618	0.7438
423.31	0.7477	0.9690	0.9717	0.6794
423.27	0.7485	0.9691	0.9718	0.6789
421.69	0.7787	0.9748	0.9780	0.6622
420.38	0.8048	0.9791	0.9828	0.6484
419.3	0.8274	0.9825	0.9862	0.6366
418.81	0.8368	0.9838	0.9889	0.6325

416.68	0.8856	0.9898	0.9936	0.6081
415.47	0.9148	0.9929	0.9961	0.5947
414.63	0.9355	0.9948	0.9978	0.5856
413.83	0.9562	0.9966	0.9990	0.5767
413.09	0.9763	0.9983	0.9995	0.5681
412.23	1.0000	1.0000	1.0003	-
ethylbenzene (1) + trichlorobenzene (2)				
486.16	0.0000	0.0000	-	1.0000
461.41	0.2253	0.5825	0.7659	0.9946
453.43	0.2983	0.6989	0.8189	0.9803
445.06	0.3864	0.7970	0.8641	0.9534
438.86	0.4571	0.8521	0.8974	0.9386
436.16	0.4901	0.8724	0.9118	0.9337
428.13	0.6031	0.9231	0.9481	0.9207
424.21	0.6646	0.9424	0.9664	0.9233
421.68	0.7086	0.9536	0.9766	0.9273
419.33	0.7536	0.9634	0.9844	0.9332
418.06	0.7794	0.9683	0.9882	0.9380
415.73	0.8308	0.9772	0.9932	0.9497
414.63	0.8566	0.9812	0.9953	0.9576
414.06	0.8704	0.9833	0.9962	0.9624
412.99	0.8976	0.9871	0.9974	0.9726
411.74	0.9313	0.9916	0.9980	0.9872
409.3	1.0000	1.0000	1.0003	-

^a Standard uncertainties u are $u(T) = 0.05$ K, $u(P) = 0.03$ kPa, and $u(x_1) = u(y_1) = 0.0051$.

Table 4. Thermodynamic consistency check of Wisniak area test

system	Wisniak point test		Wisniak area test			ΔH_i° (kJ/mol)	
	min L_k/W_k	max L_k/W_k	L	W	D		
m-xylene + ethylbenzene	1.00	1.06	0.46	0.44	2.05	m-xylene	36.11
m-xylene + trichlorobenzene	0.93	0.96	8.15	8.61	2.75	ethylbenzene	35.62
ethylbenzene + trichlorobenzene	0.92	0.94	8.14	8.66	3.14	trichlorobenzene	43.88

Table 5. The thermodynamic model parameters of Wilson, NRTL and UNIQUAC for the three binary systems

Binary Systems					
model	model parameters				
	α_{ij}	α_{ji}	b_{ij}	b_{ji}	α
m-xylene + ethylbenzene					
Wilson	-4.23795	14.08	1927.14	-6062.04	0.3
NRTL	-2.84456	-2.10822	1524.22	605.47	
UNIQUAC	4.72323	-1.98606	-2129.37	963.33	
m-xylene + trichlorobenzene					
Wilson	0.0743115	-19.1349	538.97	6844.13	0.3
NRTL	-0.247901	1.8484	1218.19	-1533.45	
UNIQUAC	-3.1134	0.654066	771.387	79.8784	
ethylbenzene + trichlorobenzene					

Wilson	2.92405	0.240872	-953.764	-423.829	
NRTL	-0.906156	-2.64009	721.874	787.409	0.3
UNIQUAC	-0.0540462	0.910056	-114.064	-258.006	

Table 6. The RMSD and the AAD of T, P, x, y for three binary systems

model	RMSD				AAD			
	$\delta(T)$	$\delta(P)$	$\delta(x_1)$	$\delta(y_1)$	$\sigma(T)$	$\sigma(P)$	$\sigma(x_1)$	$\sigma(y_1)$
m-xylene + ethylbenzene								
Wilson	0.00	0.00	1.9149E-06	0.0002	0.00	0.00	1.5556E-06	0.0002
NRTL	0.00	0.00	5.7735E-07	0.0001	0.00	0.00	3.3333E-07	0.0000
UNIQUAC	0.00	0.00	1.2019E-06	0.0001	0.00	0.00	8.8889E-07	0.0001
m-xylene + trichlorobenzene								
Wilson	0.24	0.09	4.0372E-04	0.0034	0.20	0.08	1.9416E-04	0.0022
NRTL	0.19	0.07	1.6845E-04	0.0015	0.15	0.06	8.5105E-05	0.0008
UNIQUAC	0.22	0.08	3.0049E-04	0.0024	0.18	0.07	1.3979E-04	0.0014
ethylbenzene + trichlorobenzene								
Wilson	0.20	0.09	1.8197E-04	0.0009	0.16	0.07	1.3365E-04	0.0006
NRTL	0.25	0.11	2.8859E-04	0.0004	0.20	0.09	1.9835E-04	0.0003
UNIQUAC	0.20	0.09	1.8537E-04	0.0008	0.16	0.07	1.3359E-04	0.0006

Table 7. Isobaric VLE Data of Ternary System m-xylene (1) + ethylbenzene (2) + trichlorobenzene (3) at 101.3 kPa^a

T/K	x_1	x_2	y_1	y_2	α
412.17	0.1036	0.8703	0.1013	0.8905	1.0464
414.3	0.1705	0.7995	0.1694	0.8205	1.0330
416.64	0.2611	0.6994	0.2571	0.7290	1.0584
418.74	0.4188	0.5482	0.4158	0.5712	1.0496
419.15	0.6046	0.3515	0.6094	0.3747	1.0578
418.3	0.6941	0.2564	0.7081	0.2756	1.0534
415.91	0.8281	0.1253	0.8497	0.1364	1.0605
417.4	0.7849	0.1513	0.8166	0.1653	1.0505
421.06	0.6446	0.2653	0.6776	0.2951	1.0579
422.45	0.5625	0.3530	0.5828	0.3889	1.0632
423.48	0.3981	0.5102	0.4083	0.5594	1.0689
425.63	0.3981	0.4666	0.4230	0.5320	1.0732
424.71	0.5838	0.2702	0.6386	0.3190	1.0793
422.76	0.6907	0.1347	0.7939	0.1652	1.0672
432	0.4789	0.2990	0.5549	0.3743	1.0802
441.47	0.3844	0.2828	0.4838	0.3897	1.0948
440	0.4702	0.1624	0.6378	0.2407	1.0928
449.4	0.4104	0.0954	0.6362	0.1637	1.1072
451.77	0.1623	0.3251	0.2358	0.5255	1.1124
442.68	0.0774	0.4291	0.1177	0.7260	1.1133
462.63	0.1149	0.2907	0.1683	0.4757	1.1177
462.34	0.2686	0.1467	0.4078	0.2491	1.1183
460.4	0.3346	0.0582	0.5744	0.1126	1.1263

473.35	0.2037	0.0839	0.3181	0.1470	1.1219
472.25	0.1194	0.1563	0.1847	0.2734	1.1305
472.09	0.1906	0.1150	0.2879	0.1988	1.1453
470.6	0.2195	0.0858	0.3527	0.1590	1.1530
478.55	0.0996	0.0754	0.1555	0.1368	1.1630
480.2	0.0864	0.0624	0.1348	0.1140	1.1718

^a Standard uncertainties u are $u(T) = 0.05$ K, $u(P) = 0.03$ kPa, and $u(x_1) = u(y_1) = 0.0051$.

Table 8. Deviations of estimated and experimental values of the three models for the ternary system of m-xylene (1) + ethylbenzene (2) + trichlorobenzene (3)

model	$\Delta_{\max} T^a/\text{K}$	$\Delta_{\max} y_1^b$	$\Delta_{\max} y_2$	$\Delta_{\max} y_3$	$\delta T^c/\text{K}$	δy_1^d	δy_2	δy_3
Wilson	1.67	0.0657	0.0671	0.0420	0.88	0.0388	0.0384	0.0119
NRTL	1.67	0.0657	0.0671	0.0420	0.40	0.0406	0.0395	0.0168
UNIQUAC	1.98	0.0687	0.0758	0.0461	0.89	0.0395	0.0392	0.0126

$$^a \Delta_{\max} T = \max |T_i^{\text{exp}} - T_i^{\text{est}}|$$

$$^b \Delta_{\max} y_i = \max |y_i^{\text{exp}} - y_i^{\text{est}}|$$

$$^c \delta T = \left[1/N \times \sum_{i=1}^N (T_i^{\text{exp}} - T_i^{\text{est}})^2 \right]^{1/2}$$

$$^d \delta y_i = \left[1/N \times \sum_{i=1}^N (y_i^{\text{exp}} - y_i^{\text{est}})^2 \right]^{1/2}$$

Figure 1. Schematic diagram of the modified Rose VLE still: (1) precision thermometer; (2) equilibrium chamber; (3) riser; (4) liquid sampling port; (5) heating device; (6) boiling chamber; (7) vapor condensate sampling point; (8) defresis area; (9) condenser

Figure 2. Isobaric VLE y-x phase diagram for the binary system water (1) + acetic acid (2) at 101.3 kPa. ●, experimental data; ○, literature results; —, fitted curve of literature data

Figure 3. Isobaric VLE T-x-y diagram for system m-xylene (1) + ethylbenzene (2) at 101.3 kPa. Black □ and ■, experimental x_1 and y_1 ; —, calculated with Wilson model; ---, calculated with NRTL model; ···, calculated with UNIQUAC model; red □ and ■, x and y , of Rodrigues et al. at 100.65 kPa

Figure 4. Isobaric VLE T-x-y diagram for system m-xylene (1) + trichlorobenzene (2) at 101.3 kPa. Black $\square$ and $\blacksquare$, experimental x_1 and y_1 ; —, calculated with Wilson model; ---, calculated with NRTL model; $\cdots$, calculated with UNIQUAC model

Figure 5. Isobaric VLE T-x-y diagram for system ethylbenzene (1) + trichlorobenzene (2) at 101.3 kPa. Black $\square$ and $\blacksquare$, experimental x_1 and y_1 ; —, calculated with Wilson model; ---, calculated with NRTL model; $\cdots$, calculated with UNIQUAC model

(a)

(b)

(c)

Figure 6. (a) L/W coefficients of the Wisniak test for m-xylene (1) + ethylbenzene (2) system at 101.3 kPa. (b) m-xylene (1) + trichlorobenzene (2). (c) ethylbenzene (1) + trichlorobenzene (2)

(a)

(b)

(c)

Figure 7. (a) The relative volatility curve of the binary system m-xylene (1) + ethylbenzene (2). ■, experimental relative volatility; Black —, calculated by NRTL model; Red ---, $\pm 1\%$ (a) or $\pm 5\%$ (b and c) deviations from the calculated value. (b) m-xylene (1) + trichlorobenzene (2). (c) ethylbenzene (1) + trichlorobenzene (2)

(a)

(b)

(c)

Figure 8. (a) Percentage errors of model K_1 -values of the binary system m-xylene (1) + ethylbenzene (2). ■, errors of model K_1 -values. (b) m-xylene (1) + trichlorobenzene (2). (c) ethylbenzene (1) + trichlorobenzene (2)

Figure 9. Comparison of experimental results and model estimation results of m-xylene (1) + ethylbenzene (2) + trichlorobenzene (3) system