Vapor−Liquid Equilibria Data for Binary Systems of Ethylbenzene + Xylene Isomers at 100.65 kPa

Willias L. Rodrigues,[†] Silvana Mattedi,*,[†] and João C. N. Abreu[‡]

Chemical Engineering Department, Federal University of Bahia − UFBA, Rua Aristides Novis no. 02, Federação, CEP 40210-630, Salvador-BA, Brazil, and BRASKEM − Insumos Básicos, Rua Eteno no. 1361, Pólo Petroquímico, CEP 42810-000, Camaçarí-BA, Brazil

Vapor−liquid equilibria data for binary mixture of ethylbenzene + xylene isomers were obtained isobarically with a modified Fischer cell at 100.65 kPa. Temperatures were measured with a resolution of ±0.001 K, and vapor- and liquid-phase compositions were analyzed with a gas chromatograph. The data obtained were considered to be thermodynamically consistent according to the Van Ness and Fredenslund test. Pure vapor pressures for the compounds are also reported. Interaction parameters for the most used activity coefficient models and cubic equations were obtained through data fitting performed with Aspen Plus 10.1.

Introduction

Ethylbenzene and xylene isomers are of great importance in the petrochemical industry because these substances are the basis of the synthesis of many organic compounds. For example, ethylbenzene is dehydrogenated to styrene and *p*-xylene is oxidized to teraphthalic or dimethylteraphthalic acid as the first stage in the production of polyester. Xylenes were normally produced as a mixed stream containing mainly *p*-xylene, *m*-xylene, *o*-xylene, and ethylbenzene. The separation of C8 aromatic compounds by distillation is a difficult task, and the columns usually have more than 200 stages and a high reflux ratio, owing to the low relative volatility among the compounds and the high degree of purity requested for the final commercial products. For the rigorous simulation and optimization of this separation process, it is necessary to describe the vapor−liquid equilibria (VLE) accurately.

Nevertheless, there are few literature data for binary systems of ethylbenzene and xylene isomers. *T*−*x* isobaric data for ethylbenzene + *p*-xylene at four different pressures (500, 760, 1250, and 1500 mmHg) are published.[1] Isobaric data at (6.66 and 26.66) kPa for ethylbenzene + *m*-xylene, *p*-xylene + *o*-xylene, and *m*-xylene + *o*-xylene are also reported.[2,3] Binary data for C8 compounds with *n*-heptane, 1-hexane, and cyclohexane at 101.3 kPa are also present in the literature.[4−6] In previous work, we obtained isobaric data for binary systems of *o*-xylene + *m*-xylene, *p*-xylene + *m*-xylene, and *o*-xylene + *p*-xylene at 100.65 kPa.[7]

In this article, experimental data for vapor−liquid equilibria for binary systems of ethylbenzene + xylene isomers at 100.65 kPa are reported. Vapor pressure measurements were performed a priori for all four substances. Experimental data were fitted using Aspen Plus 10.1 to obtain the binary interaction parameters for the most used activity coefficient models and for the classic mixing rules of two cubic equations of state.

Experimental Section

Materials. The xylenes used in this work were supplied by BRASKEM − Insumos Básicos S.A (Camaçari-BA, Brazil), whereas EDN−Estireno do Nordeste S.A (Camaçari-BA, Brazil) supplied the ethylbenzene. The *m*-xylene and the *o*-xylene were purified by means of a spinning band distillation system from BR Instrument Corporation. This equipment is used for the purification of solvents and the preparation of chromatographic patterns in a process consisting basically of distillation with a high reflux ratio (>200). *p*-Xylene was purified by crystallization, and ethylbenzene was used as supplied, without any extra purification, because its high purity had already been assured by chromatographic analyses. All of the compounds were passed through a molecular sieve with a 0.3 nm pore diameter, manufactured by Union Carbide, to remove any remaining free water molecules. The normal boiling points were determined using the equilibrium cell (see the following section and Figure 1 for an illustration), and densities were measured in a digital Anton Paar DMA45 by German Weber S. A. Table 1 shows that the normal boiling points and densities for the used compounds agree very closely with the literature values.[8] The chromatographic analyses showed that the minimum purity by mass was 99.8% for ethylbenzene, 99.93% for *p*-xylene, 99.75% for *m*-xylene, and 99.85% for *o*-xylene.

Apparatus and Procedure. A dynamic recirculating all-glass cell equipped with a Cottrell pump manufactured by Fisher Labor (Labodest model) was used. The apparatus is represented in Figure 1. The solenoid valves were eliminated to allow for lower disturbances in vapor−liquid equilibria during sample retrieval and for a lower variation in equilibrium temperature due to the recirculation process, as explained in detail elsewhere.[9] The equipment works with pressures varying in the range from (0.25 to 300) kPa (absolute) and temperatures up to 523.15 K. The equilibrium temperature was measured using a digital meter from Systemteknik with an accuracy of ±0.005 K and a Pt 100 sensor in the Cottrell pump. Pressure was measured with an accuracy of ±0.01 kPa. Prior to the measurements, the temperature sensor was calibrated with a set of six

* Corresponding author. E-mail: silvana@ufba.br. Fax: +55-71-2039810.
† Federal University of Bahia − UFBA.
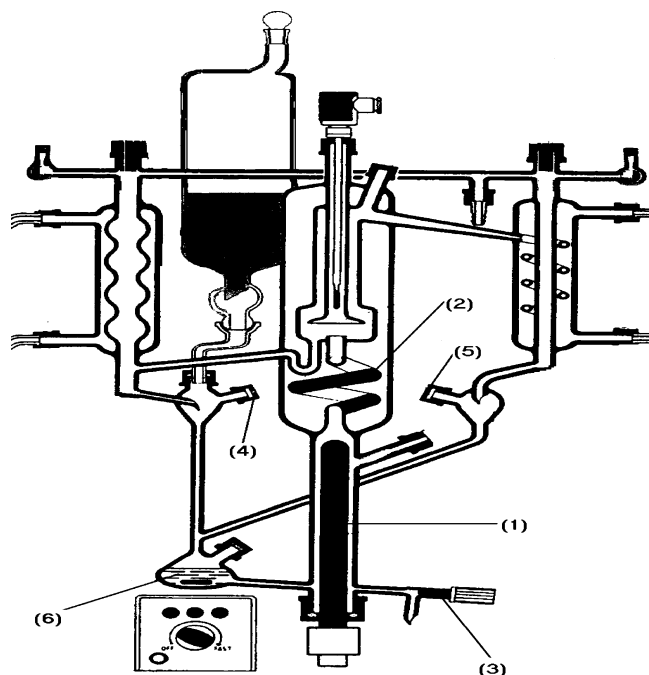‡ BRASKEM − Insumos Básicos.

Figure 1. Modified vapor−liquid equilibria Fischer cell: (1) heating bulb; (2) Cottrell pump; (3) discard valve; (4) liquid-phase sampling point; (5) vapor-phase sampling point; (6) magnetic stirrer.

Table 1. Normal Boiling Points (T_b) and Liquid Densities (ρ) at 20 °C of Pure Compounds

	T_b/K		ρ/kg m^{-3} at 20 °C	
substance	exptl	lit[a]	exptl	lit[a]
ethylbenzene	409.176	409.343	867.10	866.96
p-xylene	411.500	411.509	861.20	860.98
m-xylene	412.333	412.270	864.20	864.36
o-xylene	417.549	417.579	879.80	880.14

[a] From ref 8.

standard ASTM thermometers manufactured by ERTCO and checked with the fusion and ebullition temperatures of water.

Equilibrium were usually reached after 15 min. Mixture heating was regulated to achieve a mean speed of 30 drops/min. Samples of 0.02 μL were withdrawn from condensed vapor and liquid and analyzed with a Shimadzu gas chromatograph equipped with a flame ionization detector (FID). A 60 m × 0.32 mm × 0.5 μm capillary column (type LM100) of poly(ethylene glycol) was used, and the peak areas were integrated by a Hewlett-Packard model 3390A. Three injections of each phase were made for each point, and the mean value was recorded. Deviations were usually lower than 0.001 mole fraction.

Results

Experimental Data. Room pressure in the laboratory was always slightly less than normal pressure (101.325 kPa). To control the pressure better, we chose to fix a lower operating value for the binary data ($P = 100.65$ kPa), and this pressure was maintained using a vacuum controller system. However, for vapor-pressure data, nitrogen injection was used. The normal boiling points reported were actually obtained at $P = 101.32$ kPa.

Pure vapor pressures are reported in Tables 2 to 5. Relative deviations of pressure from the Antoine correlation (with parameters from ref 10) were all less than 2.6%.

Table 2. Vapor Pressure for Pure *p*-Xylene and Relative Deviation from Calculated Value Using Antoine Correlation with Parameters from Reference 10

T/K	P_{exptl}/kPa	$(P_{exptl} - P_{calcd})/P_{exptl}$/%
420.933	129.70	0.1
409.380	95.00	0.7
405.371	84.84	1.0
403.285	80.00	1.1
401.060	75.00	1.3
398.716	70.00	1.5
393.610	60.00	2.0
390.845	55.00	2.4
389.804	53.26	2.5

Table 3. Vapor Pressure for Pure *m*-Xylene and Relative Deviation from Calculated Value Using Antoine Correlation with Parameters from Reference 10

T/K	P_{exptl}/kPa	$(P_{exptl} - P_{calcd})/P_{exptl}$/%
423.344	137.30	1.5
415.535	111.80	1.1
409.400	95.00	1.3
407.504	90.00	1.1
406.500	87.74	1.3
403.252	80.00	1.2
400.957	75.00	1.2
397.712	67.97	0.8
393.343	60.00	1.2
389.844	53.54	0.4
387.844	50.00	0.3
384.298	45.00	0.3
380.805	40.36	0.6
376.315	35.00	1.1
371.486	29.94	1.7
366.305	25.00	1.8
362.450	21.82	2.0

Table 4. Vapor Pressure for Pure *o*-Xylene and Relative Deviation from Calculated Value Using Antoine Correlation with Parameters from Reference 10

T/K	P_{exptl}/kPa	$(P_{exptl} - P_{calcd})/P_{exptl}$/%
426.995	129.30	0.0
418.226	102.50	0.6
415.435	95.00	0.8
413.502	90.00	1.0
411.445	85.00	1.1
409.443	80.33	1.2
407.050	75.00	1.4
404.712	70.00	1.7
400.656	62.13	1.9
399.520	60.00	2.1
396.730	55.00	2.6

Table 5. Vapor Pressure for Pure Ethylbenzene and Relative Deviation from Calculated Value Using Antoine Correlation with Parameters from Reference 10

T/K	P_{exptl}/kPa	$(P_{exptl} - P_{calcd})/P_{exptl}$/%
417.003	124.30	0.1
412.485	110.02	0.2
407.145	95.00	0.5
405.261	90.00	0.8
403.270	85.00	1.0
401.164	80.00	1.2
398.930	75.00	1.3
397.490	71.87	1.4
394.153	65.00	1.8
391.507	60.00	1.9
387.750	53.37	2.3
385.698	50.00	2.5

Figure 2 shows a comparison of data obtained and Antoine correlation (with parameters taken from refs 1 and 10). Very good agreement is observed. The Antoine coefficients obtained for the present data are presented in Table 6.

$T-x-y$ experimental VLE data obtained for the systems ethylbenzene (1) + *p*-xylene (2), ethylbenzene (1) + *m*-xylene (2), and ethylbenzene (1) + *o*-xylene (2) at $P = 100.65$ kPa are presented in Tables 7 to 9.
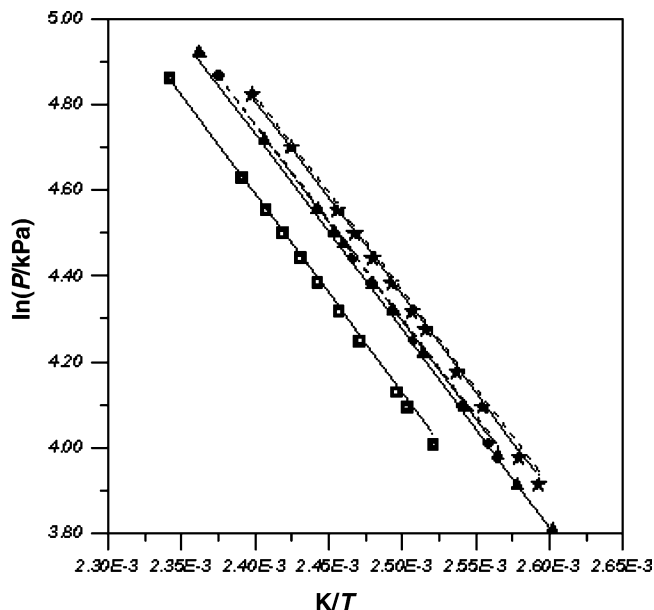
Figure 2. Vapor pressure for ethylbenzene and xylene isomers. This work: ●, *p*-xylene; ▲, *m*-xylene; □, *o*-xylene; and ★, ethylbenzene; lines are from Antoine correlations with parameters from ref 1 (- - -) and ref 10 (−).

Table 6. Parameters for the Antoine Equation^a

substances	A	B	C	rms^b/kPa
p-xylene	13.8407	3098.73	75.6906	0.04
m-xylene	13.5498	2942.34	82.3312	0.17
o-xylene	14.0164	3249.29	72.0522	0.04
ethylbenzene	14.5704	3573.27	50.4328	0.03

^{a} Obsd: $\ln P = A - B/T - C$ (P in kPa and T in K). ^{b} Root-mean-square deviation.

Table 7. Experimental VLE for the System Ethylbenzene (1) + *p*-Xylene (2) at 100.65 kPa

T/K	x_1	y_1
411.530	0.0000	0.0000
411.344	0.0445	0.0457
410.880	0.1606	0.1663
410.854	0.2580	0.2641
410.546	0.3734	0.3900
410.241	0.4907	0.5173
409.949	0.6010	0.6203
409.845	0.6988	0.7018
409.712	0.7604	0.7658
409.508	0.8299	0.8358
409.288	0.9352	0.9354
409.228	0.9709	0.9735
409.176	1.0000	1.0000

Thermodynamic Consistency Test. To verify the quality of the obtained data, it is necessary to test whether they are thermodynamically consistent, that is, to verify whether the experimental data satisfy the Gibbs−Duhem equation. In this work, the well-known Van Ness and Fredenslund test[11,12] was used. The calculated values of absolute and root mean deviations for vapor mole fraction and pressure by the thermodynamic consistency test are presented in Table 10. All of the systems were considered to be thermodynamically consistent because the deviation in the vapor mole fraction was always less than 0.01, as recommended in the literature.[12]

Data Fitting. The studied systems form almost ideal solutions; however, for rigorous simulation of high-purity columns, mixing effects should not be neglected. Therefore, data were fitted to obtain the interaction parameters for NRTL,[13] UNIQUAC,[14] and Wilson[15] activity coefficient

Table 8. Experimental VLE for the System Ethylbenzene (1) + *m*-Xylene (2) at 100.65 kPa

T/K	x_1	y_1
412.336	0.0000	0.0000
412.070	0.0496	0.0541
411.791	0.1459	0.1494
411.468	0.2352	0.2498
411.195	0.3256	0.3340
410.815	0.4299	0.4368
410.515	0.5491	0.5571
410.249	0.6353	0.6468
409.964	0.7250	0.7380
409.529	0.8584	0.8665
409.359	0.9342	0.9369
409.179	0.9664	0.9694
409.176	1.0000	1.0000

Table 9. Experimental VLE for the System Ethylbenzene (1) + *o*-Xylene (2) at 100.65 kPa

T/K	x_1	y_1
417.593	0.0000	0.0000
416.999	0.0538	0.0687
416.183	0.1396	0.1756
415.547	0.2163	0.2690
414.940	0.2899	0.3518
413.761	0.4153	0.4869
412.790	0.5211	0.5912
412.021	0.6151	0.6753
411.405	0.6918	0.7496
410.769	0.7809	0.8267
410.679	0.8457	0.8742
409.566	0.9078	0.9309
409.321	0.9579	0.9618
409.176	1.0000	1.0000

Table 10. Thermodynamic Consistency of Experimental Data

system	$y_{calcd} - y_{exptl}$	rms^a	$(P_{calcd} - P_{exptl})$/kPa
ethylbenzene + *p*-xylene	0.0052	0.006	0.0097
ethylbenzene + *m*-xylene	0.0047	0.005	0.0033
ethylbenzene + *o*-xylene	0.0082	0.009	0.0051

^{a} Root-mean-square deviation in vapor composition.

models. The vapor phase was described by a virial equation with second virial coefficients according to the Hayden and O'Connell method.[16] Because the system is apolar with very similar components, the regression of the binary interaction parameters for classic mixing rules for the cubic EOS was additionally performed. The well-known Peng−Robinson[17] and Soave−Redlich−Kwong equations, modified by Boston and Mathias,[18] were chosen. The modified form of the SRK equation was used because it represents pure vapor pressures very well, which is an important feature for systems that present small differences in pure vapor pressures. For example, it represents *p*-xylene + *m*-xylene vapor−liquid equilibria behavior, for which normal boiling points of pure compounds differ only by 0.7 K, better than the Peng−Robinson EOS.[7]

The data regression system (DRS) of the Aspen Plus 10.1 simulator was used. This system uses the Britt and Luecke method,[19] which is based on the maximum-likelihood principle. The objective function that was minimized is given by

$$F = \sum_{i=1}^{N} \left[\frac{(P_{i,\text{calcd}} - P_{i,\text{exptl}})^2}{v_P^2} + \frac{(T_{i,\text{calcd}} - T_{i,\text{exptl}})^2}{v_T^2} + \frac{(x_{i,\text{calcd}} - x_{i,\text{exptl}})^2}{v_x^2} + \frac{(y_{i,\text{calcd}} - y_{i,\text{exptl}})^2}{v_y^2} \right] \quad (1)$$

where v represents the variances from experimental mea-

Table 11. Binary Interaction Parameters for Activity Coeficient Models and Mean Deviation for Calculated Bubble Pressure and Composition

	parameters				
models	A_{ij}/J mol^{-1}	A_{ji}/J mol^{-1}	C_{ij}	$(P_{calcd} - P_{exptl})/P_{exptl}$/%	$y_{calcd} - y_{exptl}$
	Ethylbenzene (1) + *p*-Xylene (2)				
NRTL	461.72	−342.96	0.30	0.048	0.002
UNIQUAC	−243.35	187.08	187.08	0.048	0.002
Wilson	260.68	−388.75	−388.75	0.049	0.002
	Ethylbenzene (1) + *m*-Xylene (2)				
NRTL	477.03	−351.31	0.30	0.050	0.005
UNIQUAC	−259.85	196.70		0.048	0.005
Wilson	285.49	−446.89		0.049	0.005
	Ethylbenzene (1) + *o*-Xylene (2)				
NRTL	488.50	−358.22	0.30	0.029	0.009
UNIQUAC	−279.13	207.84		0.023	0.009
Wilson	305.37	−497.37		0.038	0.009

Table 12. Binary Interaction Parameters for Classic Mixing Rules Applied to Cubic EOS and for Calculated Bubble Pressure and Composition

system	k_{ij}	$y_{calcd} - y_{exptl}$	$(P_{calcd} - P_{exptl})/P_{exptl}$/%
Peng−Robinson EOS[a]			
ethylbenzene + *p*-xylene	0.00149	0.0044	0.0314
ethylbenzene + *m*-xylene	0.00215	0.0033	0.30×10^{-3}
ethylbenzene + *o*-xylene	0.00183	0.0074	0.0012
SRK EOS Modified by Boston and Mathias[b]			
ethylbenzene + *p*-xylene	0.00164	0.0011	0.0318
ethylbenzene + *m*-xylene	0.00073	0.0048	0.30×10^{-3}
ethylbenzene + *o*-xylene	0.00066	0.0093	0.0012

[a] Reference 17. [b] Reference 18.

surements. The variances for pressure and temperature were estimated from accuracies (±0.01 kPa and ±0.005 K), whereas the variances of liquid- and vapor-phase compositions were calculated from the experimental data (deviations from the recorded mean value, which was usually lower than 0.001 mole fraction). Table 11 presents the estimated values for the interactions parameters for activity coefficient models as well as the values of the mean deviation between the experimental and calculated pressure and vapor-phase composition. The binary interaction parameters for classic mixing rules of cubic equations of state are presented in Table 12 along with the absolute mean deviation between experimental and predicted values for each variable. Both EOSs are able to represent these systems very well because deviations in bubble pressure and composition are very low for all studied systems.

Figure 3 shows the comparison of the data obtained for ethylbenzene + *p*-xylene data with the results reported by Chianese and Marelli[1] for 101.3 kPa (760 mmHg). The data reported by those authors[1] for other pressures and the Peng−Robinson EOS description of this system (using the interaction parameter presented in Table 12 for all pressures) are also shown in Figure 3. It was observed that in the *p*-xylene-rich region the dew curve reported by Chianese and Marelli[1] for 101.3 kPa is lower than that found in the present investigation for 100.65 kPa. This discrepancy is due to the fact that Chianese and Marelli[1] used *p*-xylene directly with no further purification whereas the *p*-xylene used in this work was purified by crystallization and presents an attested purity of 99.93%. Moreover, Chianese and Marelli[1] report the use of thermometers with a resolution 10 times smaller than that of the thermometer used in the present work. Predictions obtained with the Peng−Robinson EOS follow the same trend for all pressures and yields slightly higher dew curves. The obtained results show that the EOS is able not only to correlate the
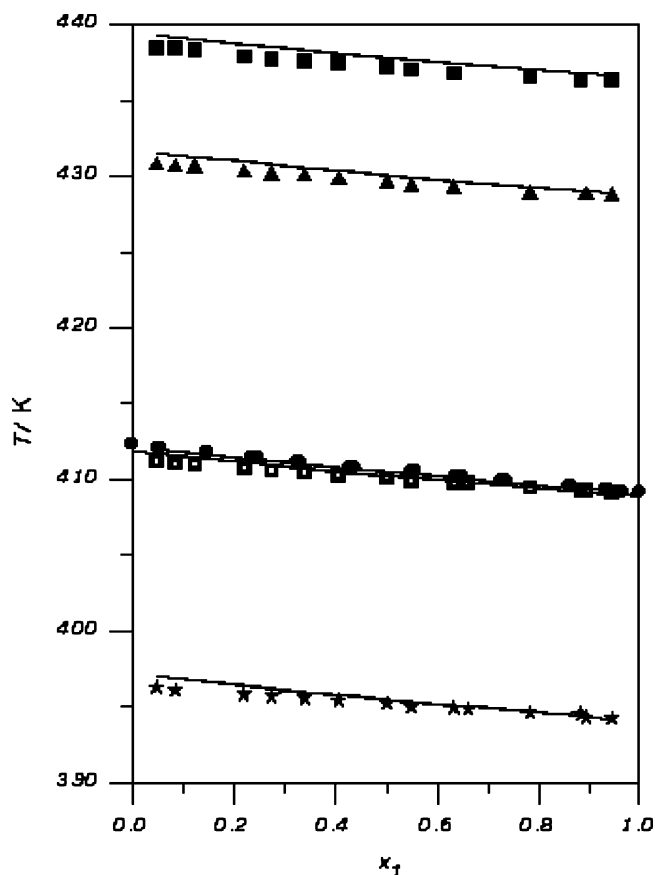

Figure 3. Vapor−liquid equilibria for ethylbenzene (1) + *p*-xylene (2) at different pressures. ●, This work at 100.65 kPa; ★, □, ■, and ▲, data from Chianese and Marelli[1] at (500, 760, 1250, and 1500) mmHg, respectively; −, bubble temperature and vapor compositions calculated by the Peng−Robinson EOS with $k_{ij} = 0.00149$.

data but also to predict the phase equilibria behavior at different pressures. Similar results are obtained with the modified Soave−Redlich−Kwong EOS.

Conclusions

In this work, experimental isobaric VLE data for three binary systems of ethylbenzene + xylene isomers obtained at 100.65 kPa are reported. Each system presents a low relative volatility, and the normal boiling points of the pure compounds have a maximum difference of 6 K for all three systems studied. Data were obtained in a modified Fischer cell, with equilibrium usually reached after 15 min, and samples for vapor and liquid phases were analyzed by gas chromatography.

The data were considered to be thermodynamically consistent according to the Van Ness and Fredenslund[11,12] point test. The binary interaction parameters were fitted to experimental data using the Aspen Plus 10.1 simulator, and the parameters for the NRTL, UNIQUAC, and Wilson models are presented. Because the studied systems are nonpolar, they were also modeled by cubic equations of state with classic mixing rules. The Peng−Robinson and the modified[18] Soave−Redlich−Kwong equations were used. It is shown that both cubic EOSs with classic mixing rules are able to represent all of the systems satisfactorily, presenting very low values for the absolute mean deviation between the experimental and the predicted values.

The experimental data obtained for ethylbenzene + *p*-xylene VLE at 100.65 kPa were compared with the results reported by Chianese and Marelli[1] at a slightly higher pressure (101.3 kPa). It was observed that their dew curve is lower than that obtained in the present work in the *p*-xylene-rich region. However, this discrepancy is credited to the lower purity of the reagents used by those authors and to the higher uncertainties reported in their temperature measurements and attests the improved reliability of the present results in comparison to previously reported data.

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