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Isobaric Vapor–Liquid Equilibria of *p*-Xylene + *o*-Xylene and *m*-Xylene + *o*-Xylene Systems at 6.66 and 26.66 kPa

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Vapor–liquid equilibrium data were obtained for systems of *o*-xylene with *p*- and *m*-xylenes at 6.66 and 26.66 kPa. The activity coefficients were found to be thermodynamically consistent. They were equally well correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations. The parameters of these equations are given.

Introduction

Xylenes are C_8 benzene homologues with the molecular formula C_8H_{10}. The three xylene isomers differ in the positions of two methyl groups on the benzene ring. Mixed xylenes are obtained from certain petroleum fractions by catalytic reforming or hydroforming (*1*). The catalytic reforming of a selected naphta cut yields a reformate rich in benzene, toluene, and xylenes. By a combination of extraction and distillation processes, a mixed xylene fraction is produced.

The xylene fraction separated from the reformate may be sold as such or further concentrated by distillation. If separation into pure isomers is desired, several expansive methods are needful. Normally, *o*-xylene is separated first by distillation. The meta and para isomers, due to their very close boiling points, cannot allow this type of separation, and commercially it is carried out by fractional crystallization or molecular sieve adsorption (*2*). Equilibrium data of systems containing xylenes are needed for the correct design of the distillation columns and condensers.

In this work, we report vapor–liquid equilibrium (VLE) data for two of these systems, *p*-xylene + *o*-xylene and *m*-xylene + *o*-xylene, at low pressure. The equilibrium data at reduced pressures (6.66 and 26.66 kPa) were obtained to avoid high boiling temperatures, which could damage these compounds, as well as to bring information to get a more effective separation. No VLE data have been reported previously for the *p*-xylene + *o*-xylene system. For *m*-xylene + *o*-xylene two sets of data are available in the literature (*3*, *4*), but those data are at atmospheric pressure and in ref 3 were made by measuring isothermal VLE using a gas chromatographic analysis of a saturated flow of inert gas.

Experimental Section

Chemicals. Aldrich Chemical reactives were used in the experiments. *p*-Xylene and *m*-xylene (>99.0%) and *o*-xylene (>98%) were all high-purity grade. The physical properties of these components are listed in Table 1 together with literature values (*5*). Density has been measured in a digital densimeter Anton Paar DMA55, German Weber S.A., and refractive index in an Abbe refractometer, Atago 3T. The accuracies in density and refractive index measurements are ±0.000 01 g/cm³ and ±0.0002, respectively.

Apparatus and Procedure. The apparatus used in this work was an all-glass, dynamic recirculating still described by Walas (*6*), equipped with a Cottrell pump. The still (Labodest model) manufactured by Fischer Labor und Verfahrenstechnik (Germany) is capable of handling pressures from 0.25 to 400 kPa, and temeratures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact and also in contact with the temperature-sensing element. The equilibrium temperature, T, was measured with a digital Fisher thermometer with an accuracy of 0.1 K, and the pressure, P, with a digital manometer with an accuracy of 0.01 kPa. VLE data were obtained at two pressures (6.66 and 26.66 kPa) for both systems. The vapor pressures of the pure components were measured with the same recirculating still.

Table 1. Densities d, Refractive Indexes n_D, and Boiling Points T_b of the Compounds

	d(293.15 K)/(g/cm³)		n(D, 293.15 K)		T_b(26.66 kPa)/K	
compound	exptl	lit. (*5*)	exptl	lit. (*5*)	exptl	lit.[a]
p-xylene	0.860 91	0.8611	1.4950	1.4958	367.55	367.76
m-xylene	0.864 12	0.8642	1.4964	1.4972	368.45	368.63
o-xylene	0.879 67	0.8802	1.5048	1.5055	373.25	373.37

[a] Calculated using the Antoine coefficients from ref 15.

In each experiment, the work pressure was fixed and the heating and shaking system of the liquid mixture was connected. This was kept at the boiling point for about 15 min to ensure the stationary state. Once it was certain that the stationary state was reached, a sample of liquid and vapor from the Cottrell pump was taken. The extractions were carried out with special syringes which allowed us to take small volume samples in a system under partial vacuum.

Samples of 0.2 mL were withdrawn from the condensed vapor and liquid streams of the still, and were analyzed with a Hewlett-Packard 5700A gas chromatograph (GC) with a thermal-conductivity detector. The GC response peaks were integrated by using a Hewlett-Packard 3394A integrator. The GC column used was packed with 16% DC-200 methyl silicone oil and 3% Bentone-34 on Chromosorb W (80/100), of 3-m length and 1/8-in. diameter. Chromatographic analyses were carried out at 85 °C; the helium gas flow was 20 cm³/min.

The GC was calibrated with gravimetrically prepared standard solutions. A single analysis of the vapor or liquid composition by gas chromatography is frequently imprecise. However, with repeated measurements, the standard deviation of a composition analysis was usually less than 0.001 mole fraction. At least two analyses were made of each liquid and each vapor composition.

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Table 2. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, for the p-Xylene (1) + o-Xylene (2) System at Constant Pressure P

P/kPa	x_1	y_1	T/K	γ_1	γ_2
6.66	0.000	0.000	337.55		
	0.050	0.063	337.25	1.086	1.005
	0.100	0.125	337.05	0.995	1.012
	0.182	0.219	336.55	0.977	1.014
	0.263	0.310	336.15	0.996	1.008
	0.343	0.397	335.65	1.004	1.005
	0.420	0.477	335.25	1.000	1.008
	0.497	0.555	334.85	0.994	1.013
	0.577	0.633	334.45	0.991	1.017
	0.657	0.709	334.05	0.992	1.014
	0.738	0.780	333.65	0.995	1.007
	0.815	0.849	333.25	0.996	1.003
	0.895	0.915	332.85	0.997	0.999
	0.948	0.959	332.55	0.999	0.980
	1.000	1.000	332.35		
26.66	0.000	0.000	373.25		
	0.049	0.058	372.95	1.078	1.002
	0.099	0.118	372.65	1.036	1.005
	0.174	0.207	372.15	1.008	1.009
	0.251	0.293	371.65	1.002	1.010
	0.326	0.371	371.25	1.003	1.010
	0.406	0.449	370.75	1.005	1.008
	0.486	0.538	370.35	1.005	1.008
	0.569	0.618	369.85	1.004	1.010
	0.649	0.696	369.35	1.003	1.012
	0.731	0.773	368.95	1.002	1.012
	0.814	0.845	368.55	1.003	1.011
	0.907	0.916	368.05	1.002	1.018
	0.954	0.960	367.75	1.001	1.034
	1.000	1.000	367.55		

Table 3. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, for the m-Xylene (1) + o-Xylene (2) System at Constant Pressure P

P/kPa	x_1	y_1	T/K	γ_1	γ_2
6.66	0.000	0.000	337.55		
	0.054	0.064	337.35	1.075	1.004
	0.103	0.123	337.15	1.017	1.008
	0.185	0.218	336.75	1.001	1.010
	0.267	0.308	336.35	1.009	1.008
	0.351	0.397	335.95	1.011	1.007
	0.431	0.481	335.65	1.007	1.010
	0.509	0.557	335.25	1.003	1.013
	0.586	0.631	334.95	1.003	1.013
	0.660	0.703	334.65	1.006	1.008
	0.739	0.774	334.25	1.009	1.001
	0.818	0.845	333.95	1.008	1.005
	0.897	0.913	333.65	1.004	1.034
	0.947	0.955	333.45	1.001	1.068
	1.000	1.000	333.25		
26.66	0.000	0.000	373.25		
	0.047	0.056	372.95	1.090	1.004
	0.097	0.114	372.75	1.007	1.009
	0.178	0.206	372.35	0.985	1.012
	0.259	0.293	371.95	1.003	1.007
	0.341	0.381	371.55	1.016	1.002
	0.425	0.468	371.05	1.015	1.002
	0.496	0.539	370.75	1.010	1.007
	0.574	0.615	370.35	1.006	1.011
	0.655	0.692	369.95	1.006	1.011
	0.735	0.765	369.65	1.008	1.008
	0.808	0.832	369.25	1.008	1.008
	0.886	0.902	368.95	1.005	1.026
	0.937	0.946	368.75	1.002	1.057
	1.000	1.000	368.45		

Results and Discussion

The VLE data for both binary systems have been obtained at 6.66 and 26.66 kPa and are presented in Tables 2 and 3. The T–x–y diagram for the p-xylene (1) + o-xylene (2) is shown in Figure 1.

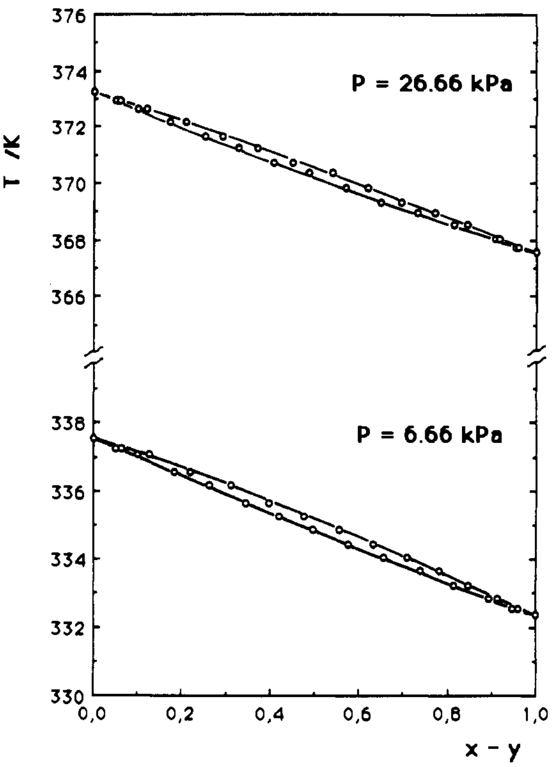

Figure 1. Vapor–liquid equilibrium temperature T of the system p-xylene (1) + o-xylene (2) at P = 6.66 and 26.66 kPa as a function of the mole fraction of component 1.

Table 4. Test of Thermodynamic Consistency of the Experimental Data Sum of the Squared Relative Deviations SSRD(P) and Mean Average Deviation MAD(y)

system	P/kPa	SSRD(P)	MAD(y)
p-xylene + o-xylene	6.66	1.42E–05	0.0022
	26.66	1.67E–05	0.0034
m-xylene + o-xylene	6.66	1.48E–05	0.0018
	26.66	1.15E–05	0.0020

The activity coefficients γ_i of the components were calculated from

$$\gamma_i = y_i \phi_i P / x_i f_i^\circ \tag{1}$$

where x_i and y_i are the liquid and vapor mole fractions in equilibrium, ϕ_i is the fugacity coefficient, and f_i° is the liquid fugacity in the standard state.

The fugacity coefficients calculated on the basis of the Redlich–Kwong equation of state (7), with the modification introduced by Soave (8), are nearly unity. If we determine f_i° according to the standard state of Lewis and Randall and considering the Poynting factor as unity as the experimental conditions of this work (9), then eq 1 is reduced to

$$\gamma_i = y_i P / x_i P_i^\circ \tag{2}$$

where the vapor pressures P_i° were calculated with the equation

$$\ln(P_i^\circ/\text{kPa}) = A_i + \frac{B_i}{T/\text{K}} + C_i \ln(T/\text{K}) + D_i (T/\text{K})^{E_i} \tag{3}$$

using the coefficients given in ref 10. The γ_i values are listed in Tables 2 and 3.

The thermodynamic consistency of the experimental data was checked by means of the point-to-point test of Van Ness et al. (*11*), modified by Fredenslund et al. (*12*), using a fifth-order Legendre polynomial where the objective function was the sum of the squared relative deviations in total pressure,

Table 5. Correlation Parameters for Activity Coefficients, Activity Coefficients at Infinite Dilution γ_i^∞, and Mean Absolute Deviations MAD(y) and MAD(T)

P/kPa		A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	MAD(y)	MAD(T)/K
			p-Xylene (1) + *o*-Xylene (2)					
6.66	Margules	0.1094[a]	0.0032[a]		1.116	1.003	0.0042	0.17
	Van Laar	0.1093[a]	0.0037[a]		1.116	1.004	0.0016	0.08
	Wilson	644.75[b]	−400.28[b]		1.135	1.003	0.0021	0.10
	NRTL	−544.40[b]	779.39[b]	0.3013[a]	1.134	1.003	0.0036	0.15
	UNIQUAC	−299.98[b]	401.37[b]		1.130	1.005	0.0031	0.14
26.66	Margules	0.0600	0.0013		1.062	1.001	0.0039	0.05
	Van Laar	0.0637	0.0015		1.066	1.002	0.0025	0.15
	Wilson	539.94	−372.41		1.063	1.001	0.0033	0.07
	NRTL	−474.23	612.45	0.3007	1.052	1.003	0.0033	0.06
	UNIQUAC	−269.86	337.52		1.059	1.002	0.0066	0.24
			m-Xylene (1) + *o*-Xylene (2)					
6.66	Margules	0.0673	0.0521		1.070	1.054	0.0033	0.09
	Van Laar	0.0748	0.0467		1.078	1.048	0.0017	0.05
	Wilson	201.75	−137.89		1.071	1.051	0.0027	0.07
	NRTL	−40.539	87.918	0.3005	1.072	1.069	0.0038	0.11
	UNIQUAC	−113.18	136.26		1.071	1.055	0.0033	0.09
26.66	Margules	0.0348	0.0288		1.035	1.029	0.0014	0.07
	Van Laar	0.0480	0.0262		1.049	1.027	0.0017	0.07
	Wilson	288.61	−216.49		1.045	1.024	0.0016	0.07
	NRTL	−46.536	72.865	0.3003	1.035	1.034	0.0014	0.07
	UNIQUAC	−150.88	176.06		1.043	1.028	0.0031	0.12

[a] Dimensionless. [b] Calories per mole.

Table 6. Relative Volatilities (α) Estimated by a Polynomial Fit and Standard Deviations $\sigma(\alpha)$

system	P/kPa	α	$\sigma(\alpha)$
p-xylene + *o*-xylene	6.66	1.252	0.006
	26.66	1.210	0.024
m-xylene + *o*-xylene	6.66	1.225	0.005
	26.66	1.196	0.003

SSRD(P):

$$\mathrm{SSRD}(P) = \sum\left(\frac{P_{\mathrm{exptl}} - P_{\mathrm{calcd}}}{P_{\mathrm{exptl}}}\right)^2 \tag{4}$$

According to this test, the data are considered consistent if the mean absolute deviation in y, MAD(y), is less than 0.01. In this work, for all cases the MAD(y) values obtained satisfactorily fulfill this condition as we can see in Table 4, thereby showing them to be thermodynamically consistent.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (*13*). The adjustable parameters A_{12}, A_{21}, and α_{12} for the correlation data, mean absolute deviations, and activity coefficients at infinite dilution γ_i^∞ for the two systems are listed in Table 5. Mean absolute deviations between experimental and calculated temperatures, MAD(T), and vapor compositions, MAD(y), are of the order of estimated experimental uncertainties.

For fitting the binary parameters, the Rosenbrok method (*14*) was used to minimize the following objective function, using the activity coefficients obtained from the consistency test as experimental values:

$$F = \sum\left(\frac{\gamma_{\mathrm{exptl}} - \gamma_{\mathrm{calcd}}}{\gamma_{\mathrm{exptl}}}\right)^2 \tag{5}$$

The relative volatiles α calculated by means of eq 6 can be seen in Table 6; in both systems, the separation is more favorable at reduced pressures:

$$\alpha = [\mathrm{d}y_{\mathrm{exptl}}/\mathrm{d}x_{\mathrm{exptl}}]_{x_{\mathrm{exptl}}\to 0} \tag{6}$$

Conclusions

The following conclusions can be extracted from the results obtained in this work: Vapor–liquid equilibria for these binary systems have been measured and found to be thermodinamically consistent. The data are used to determine binary interaction parameters using the Margules, Van Laar, Wilson, NRTL, and UNIQUAC models. All models represent the data quite well. The investigated systems show small deviations from ideality, as can be seen from the activity coefficients at infinite dilution (Table 5). The vapor–liquid equilibrium is slightly influenced by pressure.

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