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Isobaric Vapor−Liquid Equilibria for Binary and Ternary Systems Composed of 1,4-Dimethylbenzene, 1,3-Dimethylbenzene, and 1,2-Dimethylbenzene at 6.66 and 26.66 kPa

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Vapor−liquid equilibrium data were obtained for the 1,4-dimethylbenzene + 1,3-dimethylbenzene binary system and the 1,4-dimethylbenzene + 1,3-dimethylbenzene + 1,2-dimethylbenzene ternary system at the isobaric conditions of 6.66 and 26.66 kPa. The activity coefficients in the binary system were found to be thermodynamically consistent, and the results were equally well correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations. The binary interaction parameters obtained from this and our previous studies are used to predict the vapor−liquid equilibrium for the ternary mixture using the above models.

Introduction

Mixed xylenes (dimethylbenzenes) are largely derived from petroleum and are a part of the commercial mixtures of liquid fuels for engines, due to their high octane index. These compounds are important in the petrochemical industry, since they are the basis for the synthesis of many organic compounds (*1*). 1,4-Dimethylbenzene (*p*-xylene) is used to produce polyesters from terephthalic acid or dimethyl terephthalate intermediates, and likewise 1,2-dimethylbenzene (*o*-xylene) is oxidized to phthalic anhydride and later converted into plasticizers.

The separation of a mixture of xylenes is technically quite complicated due to the similarity of their physical properties (*2*). Vapor−liquid equilibrium (VLE) studies on mixtures of the xylenes are needed for the correct design of the distillation columns. For multicomponent mixtures, it is not economical to make all the measurements necessary for a complete description of the systems. VLE can be calculated from the related binary and pure component data (*3*), with a minimum of ternary mixture experimental data.

The binary mixtures of *p*-xylene + *o*-xylene and *m*-xylene + *o*-xylene at low pressure have been investigated previously (*4*). In this work, we report VLE measurement on the *p*-xylene + *m*-xylene binary system and the *p*-xylene + *m*-xylene + *o*-xylene ternary system at low pressure. No VLE data have been reported previously for the ternary system. For *p*-xylene + *m*-xylene two sets of data are available in the literature (*5, 6*), but those data are at atmospheric pressure. Wilson, NRTL, and UNIQUAC binary parameters of these systems have been used to compare with the experimental data in the ternary system.

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 (*7, 17*). The density was measured in a digital densimeter, Anton Paar DMA55, German Weber S.A., and the refractive index in an Abbe refractometer, Atago 3T. The accuracies in density and refractive index measurements are ±0.000 01 g/cm^3 and ±0.0002, respectively.

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

	ϱ(293.15 K)/(g/cm^3)		n_D(293.15 K)		T_b(26.66 kPa)/K	
compound	exp	lit. (*7*)	exp	lit. (*7*)	exp	lit. (*17*)
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

Apparatus and Procedure. The apparatus used in this work was an all-glass, dynamic recirculating still described by Walas (*8*), equipped with a Cottrell pump. The still (Labodest model), manufactured by Fischer Labor and Verfahrenstechnik (Germany), is capable of handling pressures from 0.25 to 400 kPa and temperatures 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.

In each experiment, the work pressure was fixed and the heating and shaking system of the liquid mixture was connected. The system was kept at the boiling point for about 15 min to ensure the equilibrium. Once it was sure that the equilibrium was reached, a sample of liquid and vapor 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 5890 S-II gas chromatograph (GC) with a flame ionization detector. The GC response peaks were integrated by using a Hewlett-Packard 3396 integrator. The GC column used was a fused silica capillary column, SUPELCOWAX 10, of 60-m length and 0.2-mm internal diameter. Chromatographic analyses were carried out at 373 K.

The GC was calibrated with gravimetrically prepared standard solutions. A single analysis of the vapor or liquid composition by gas chromatography is frequently impre-

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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) + *m*-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	333.25		
	0.084	0.087	333.15	0.992	1.006
	0.155	0.160	333.10	0.979	1.008
	0.244	0.251	333.05	0.998	1.003
	0.331	0.339	332.95	1.003	1.001
	0.409	0.419	332.85	0.997	1.004
	0.490	0.500	332.80	0.992	1.009
	0.571	0.580	332.75	0.993	1.008
	0.653	0.664	332.65	0.996	1.002
	0.736	0.746	332.60	0.997	1.000
	0.816	0.824	332.50	0.995	1.008
	0.896	0.899	332.45	0.995	1.010
	0.948	0.948	332.40	0.997	0.975
	1.000	1.000	332.35		
26.66	0.000	0.000	368.45		
	0.083	0.085	368.35	1.027	1.004
	0.155	0.158	368.30	1.001	1.007
	0.243	0.249	368.20	0.999	1.007
	0.330	0.336	368.15	1.003	1.006
	0.409	0.417	368.05	1.005	1.005
	0.490	0.497	368.00	1.004	1.006
	0.571	0.579	367.90	1.003	1.007
	0.653	0.661	367.85	1.003	1.007
	0.738	0.743	367.75	1.003	1.007
	0.817	0.822	367.70	1.003	1.008
	0.895	0.899	367.65	1.001	1.016
	0.948	0.948	367.60	1.000	1.027
	1.000	1.000	367.55		

cise. 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.

Results and Discussion

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 (*9*), with the modification introduced by Soave (*10*), are nearly unity. If we determined f_i° according to the standard state of Lewis and Randall and considering the Poynting factor as unity at the experimental conditions of this work (*11*), 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

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

using the coefficients given in ref 12.

Binary System. The VLE data for the binary system have been obtained at 6.66 and 26.66 kPa, and the γ_i values are presented in Table 2. The thermodynamic consistency of the experimental data was checked by means of the point-to-point test of Van Ness et al. (*13*), modified by Fredenslund et al. (*14*), using a fifth-order Legendre polynomial where the objective function was the sum of the squared relative deviations in total pressure, SSRD(*P*). According to this test, the data are considered consistent if the mean absolute deviation in *y*, $\delta(y)$, is less than 0.01. In this work, for both cases $\delta(y)$ values obtained satisfactorily fulfill that condition as we can see in Table 3, thereby showing them to be thermodynamically consistent.

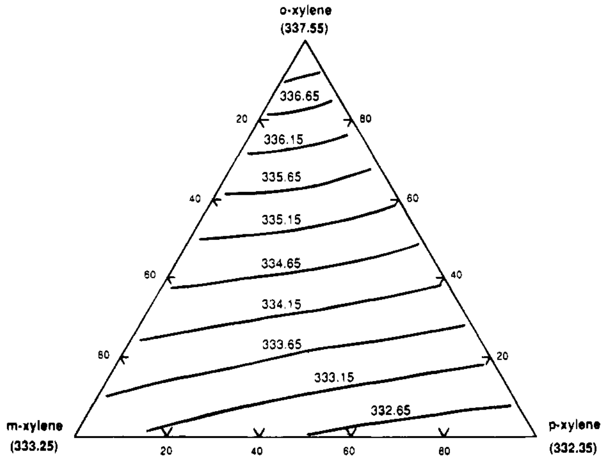

Figure 1. Vapor–liquid equilibrium isotherms for the ternary system *p*-xylene (1) + *m*-xylene (2) + *o*-xylene (3) at $P = 6.66$ kPa, using the Wilson equation, as a function of the liquid mole fraction.

Table 3. Test of the Thermodynamic Consistency of the Experimental Data Sum of the Squared Relative Deviations SSRD(*P*) and Mean Average Deviation $\delta(y)$

system	P/kPa	SSRD(P)	$\delta(y)$
p-xylene + *m*-xylene	6.66	2.41×10^{-6}	0.0015
	26.66	2.43×10^{-6}	0.0011

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (*15*). 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 system are listed in Table 4. Mean absolute deviations between experimental and calculated temperatures, $\delta(T)$, and vapor compositions, $\delta(y)$, are on the order of estimated experimental uncertainties. For fitting the binary parameters, the Rosenbrok method (*16*) was used to minimize the following objective function, using the activity coefficients obtained from the consistency test as experimental values:

$$F = \sum \left(\frac{\gamma_{\text{exp}} - \gamma_{\text{calc}}}{\gamma_{\text{exp}}} \right)^2 \tag{4}$$

This system is particularly hard because the measured temperatures vary by only 0.9 K from one end of the composition range to the other. Therefore, the vapor and liquid compositions only differ roughly 0.01 at most and are usually less than that. Consequently, the nature of this binary system is such that not much information can be obtained from the data other than the result that the system is nearly ideal. They almost certainly would not be useful for discriminating between models.

Ternary System. The VLE data for the ternary system have been obtained at 6.66 and 26.66 kPa, and the γ_i values are presented in Table 5. Many researchers have shown that multicomponent vapor–liquid equilibrium data can be predicted using a suitable model for the activity coefficients of the components and binary interaction parameters obtained from the regression of binary data. To test this, for our ternary system, we used the binary interaction parameters obtained from this study and our previous work (*4*) to predict the bubble point temperature and vapor-

Table 4. Correlation Parameters for Activity Coefficients, Activity Coefficients at Infinite Dilution γ_i^∞, and Mean Absolute Deviations $\delta(y)$ and $\delta(T)$ in *p*-Xylene (1) + *m*-Xylene (2)

P/kPa		A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	$\delta(y)$	$\delta(T)$
6.66	Margules	0.0204[a]	0.0348[a]		1.021	1.035	0.0028	0.12
	Van Laar	0.0243[a]	0.0341[a]		1.025	1.035	0.0021	0.09
	Wilson	−349.03[b]	458.38[b]		1.027	1.032	0.0022	0.10
	NRTL	501.77[b]	−402.37[b]	0.300[a]	1.027	1.030	0.0027	0.12
	UNIQUAC	320.56[b]	−281.48[b]		1.027	1.032	0.0027	0.13
26.66	Margules	0.0174	0.0208		1.017	1.021	0.0017	0.04
	Van Laar	0.0126	0.0247		1.013	1.025	0.0017	0.04
	Wilson	−394.68	486.51		1.019	1.022	0.0016	0.03
	NRTL	507.87	−423.73	0.300	1.020	1.022	0.0018	0.03
	UNIQUAC	335.70	−303.34		1.017	1.020	0.0022	0.05

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

Table 5. Vapor−Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_i, Vapor-Phase Mole Fraction y_i, Temperature T, and Activity Coefficients γ_i, for the *p*-Xylene (1) + *m*-Xylene (2) + *o*-Xylene (3) System at Constant Pressure P

x_1	x_2	y_1	y_2	T/K	γ_1	γ_2	γ_3	x_1	x_2	y_1	y_2	T/K	γ_1	γ_2	γ_3
							P = 6.66 kPa								
0.097	0.097	0.116	0.113	336.45	0.997	1.012	1.017	0.287	0.401	0.317	0.420	334.15	1.014	1.013	0.991
0.097	0.190	0.113	0.214	336.00	0.995	1.005	1.022	0.287	0.503	0.306	0.517	333.75	0.999	1.008	1.013
0.097	0.285	0.114	0.321	335.60	1.009	1.020	1.010	0.284	0.608	0.305	0.608	333.25	1.025	1.005	0.996
0.098	0.383	0.102	0.408	335.15	0.914	0.985	1.063	0.379	0.105	0.443	0.115	334.60	1.053	1.038	0.989
0.098	0.484	0.109	0.519	334.75	0.998	1.009	1.019	0.373	0.200	0.423	0.215	334.40	1.032	1.028	0.986
0.098	0.586	0.108	0.618	334.25	1.004	1.015	1.017	0.389	0.302	0.419	0.315	334.05	0.997	1.009	1.018
0.099	0.693	0.105	0.715	333.85	0.988	1.010	1.032	0.385	0.401	0.411	0.412	333.85	0.996	1.004	0.987
0.099	0.795	0.104	0.805	333.55	0.990	1.004	1.038	0.386	0.507	0.408	0.505	333.20	1.013	1.002	1.006
0.189	0.097	0.226	0.111	336.30	1.004	1.006	0.993	0.479	0.100	0.527	0.107	334.25	1.008	1.026	1.020
0.189	0.194	0.216	0.213	335.55	0.989	0.999	1.023	0.454	0.197	0.492	0.206	333.95	1.006	1.017	1.028
0.191	0.295	0.219	0.322	335.00	1.012	1.017	1.013	0.486	0.303	0.515	0.308	333.60	0.999	1.005	1.012
0.193	0.392	0.215	0.422	334.55	1.010	1.020	1.011	0.487	0.407	0.505	0.407	333.15	0.997	1.009	1.022
0.193	0.493	0.210	0.518	334.15	1.003	1.015	1.017	0.588	0.102	0.636	0.105	333.75	1.012	1.011	1.002
0.195	0.595	0.209	0.615	333.75	1.007	1.017	0.998	0.593	0.202	0.625	0.204	333.35	1.004	1.013	1.017
0.193	0.700	0.205	0.708	333.35	1.012	1.011	0.996	0.594	0.304	0.616	0.300	333.10	0.999	1.001	1.007
0.286	0.105	0.330	0.116	335.30	1.009	1.021	1.017	0.694	0.101	0.729	0.102	333.35	1.001	1.003	1.009
0.288	0.204	0.325	0.222	334.85	1.005	1.017	1.019	0.694	0.203	0.715	0.201	332.95	0.999	1.007	1.016
0.288	0.303	0.321	0.323	334.50	1.011	1.014	1.008	0.798	0.100	0.820	0.098	332.85	1.001	1.001	1.000
							P = 26.66 kPa								
0.094	0.094	0.110	0.108	372.25	1.005	1.016	1.004	0.277	0.392	0.296	0.410	369.75	0.993	1.005	1.011
0.098	0.190	0.113	0.214	371.75	1.001	1.011	1.003	0.276	0.497	0.294	0.511	369.25	1.009	1.004	0.997
0.098	0.286	0.110	0.315	371.25	0.990	1.005	1.009	0.281	0.604	0.281	0.609	368.85	0.958	1.001	1.121
0.096	0.378	0.108	0.414	370.75	1.007	1.018	1.000	0.365	0.102	0.401	0.109	370.65	0.989	0.993	1.015
0.098	0.485	0.107	0.519	370.25	0.996	1.011	1.004	0.372	0.198	0.402	0.210	370.15	0.992	1.007	1.011
0.098	0.586	0.107	0.621	369.75	1.015	1.019	0.981	0.370	0.294	0.389	0.309	369.75	0.978	1.009	1.024
0.099	0.693	0.107	0.722	369.35	1.019	1.015	0.950	0.372	0.395	0.391	0.408	369.15	0.999	1.013	1.001
0.094	0.787	0.106	0.811	368.95	1.077	1.019	0.814	0.376	0.506	0.392	0.509	368.75	1.002	1.000	0.998
0.191	0.098	0.229	0.113	371.65	1.045	1.043	0.985	0.472	0.099	0.480	0.106	370.05	0.936	1.018	1.086
0.191	0.195	0.218	0.216	371.15	1.012	1.017	0.998	0.479	0.200	0.498	0.205	369.55	0.971	0.993	1.064
0.187	0.288	0.208	0.313	370.75	0.999	1.008	1.004	0.480	0.303	0.508	0.308	369.05	1.007	1.002	0.989
0.187	0.385	0.201	0.406	370.35	0.981	0.994	1.022	0.479	0.407	0.495	0.406	368.65	0.997	0.997	1.026
0.189	0.486	0.202	0.507	369.80	0.990	1.001	1.019	0.586	0.101	0.629	0.104	369.45	1.007	0.993	0.985
0.187	0.584	0.197	0.602	369.40	0.988	1.002	1.017	0.589	0.203	0.623	0.205	368.95	1.010	1.001	0.967
0.191	0.697	0.203	0.703	368.95	1.015	0.997	0.986	0.585	0.303	0.603	0.304	368.65	0.993	1.000	0.997
0.264	0.099	0.302	0.109	371.15	1.013	1.013	1.002	0.674	0.101	0.712	0.101	369.05	1.005	0.982	0.972
0.275	0.197	0.300	0.212	370.65	0.984	1.005	1.018	0.690	0.202	0.705	0.203	368.55	0.990	1.006	1.011
0.273	0.293	0.293	0.308	370.20	0.980	0.994	1.033	0.787	0.102	0.813	0.096	368.45	1.004	0.947	0.972

phase mole fractions of the components of the ternary system. The equations used to determine the activity coefficients for any component of the ternary mixture using the Wilson, NRTL, and UNIQUAC models were taken from ref 15.

Table 6 lists the average absolute deviations δs between experimental and calculated temperatures and vapor-phase mole fractions of the components. The predictions of bubble point temperature and vapor-phase mole fraction generally agree with experiment within 0.1 K and 0.005 mole fraction, respectively. The comparison with experimental results indicates that the calculations show good agreement with data for this ternary system. After that we can predict the vapor-phase compositions and boiling points of the liquid-phase composition of the mixture at the same pressure. In Figure 1, we represent boiling isotherms calculated with the Wilson equation model.

Table 6. Correlation of Experimental Ternary Data with the Ideal Solution Equation and with Nonideal Wilson, NRTL, and UNIQUAC Equations Using Binary Data Parameters for Activity Coefficients

P/kPa		$\delta(y_1)$	$\delta(y_2)$	$\delta(T)$
6.66	Wilson	0.0025	0.0017	0.11
	NRTL	0.0030	0.0021	0.12
	UNIQUAC	0.0030	0.0022	0.14
	ideal	0.0027	0.0016	0.18
26.66	Wilson	0.0045	0.0023	0.07
	NRTL	0.0046	0.0025	0.06
	UNIQUAC	0.0046	0.0024	0.06
	ideal	0.0048	0.0022	0.08

If it is accepted that there is a truly ideal solution, then there is no question that this system has some nonidealities. Therefore, we have used the ideal solution equations to predict the ternary data, in Table 6 we list the average absolute deviations between experimental and calculated temperatures and vapor-phase mole fractions of the components, and we can see that the predicted and experimental values agree within their estimated experimental uncertainties in the same manner as those from the most sophisticated activity models.

Conclusions

The following conclusions can be extracted from the results obtained in this work: The mixtures studied showed minimum deviations from ideality. The vapor–liquid equilibrium data are slightly influenced by pressure. The binary parameters obtained in this study and in our previous work are used to predict ternary vapor–liquid equilibrium curves, in a satisfactory manner, using the same models.

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