(6) Triday, J. O. *J. Chem. Eng. Data* **1983**, *28*, 307.
(7) Triday, J. O. Chemical Engineer Thesis, Universidad Têcnica Federico Santa Maria, Valparaiso, Chile, 1977.
(8) Vera, J. H.; Prausnitz, J. M. *J. Chem. Eng. Data* **1971**, *16*, 149.
(9) Prausnitz, J. M.; Eckert, C. A.; Orye, R. V.; O'Connell, J. P. "Computer Calculations for Multicomponent Vapor-Liquid Equilibria", 1st ed.; Prentice-Hall: Englewood Cliffs, NJ, 1965.
(10) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(11) Wolfe, P. *Commun. ACM* **1959**, *2* (12), 12-3.
(12) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", API Research Project 44; American Petroleum Institute: Washington, DC, 1962.
(13) Reid, C. R.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids", 3rd ed.; McGraw-Hill: New York, 1977.

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Vapor–Liquid Equilibria in Toluene + *m*-Xylene, Toluene + *n*-Decane, and *n*-Decane + *m*-Xylene Mixtures

Bert Willman and Amyn S. Teja*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Isothermal vapor–liquid equilibria at three temperatures between 373.5 and 394.3 K were measured for the binary systems toluene + *m*-xylene, toluene + *n*-decane, and *n*-decane + *m*-xylene by using a recirculating still. The data reported were found to be thermodynamically consistent and were correlated with four well-known activity coefficient models. The maximum likelihood method was used to estimate the parameters of the models.

Introduction

As part of a continuing study of phase equilibria involving coal chemicals, isothermal vapor–liquid equilibria (VLE) were measured for the binary systems toluene + *m*-xylene, toluene + *n*-decane, and *n*-decane + *m*-xylene at three temperatures between 373.5 and 394.3 K.

Experimental Section

The VLE still that was used in this work was an all-glass Stage-Muller recirculating still described recently by Gutsche and Knapp (*1*). The prominent features of the still are shown in Figure 1 and a schematic of the whole apparatus is given in Figure 2. The important features of the still are the magnetic sampling valves, the Cottrell pump, and the silver-plated vacuum jacket. The valves allow sampling of the equilibrium phases without disrupting the operation of the still. The vacuum jacket surrounds the equilibrium chamber and prevents partial condensation of the vapor separating from the liquid at the exit from the Cottrell pump. Heating of the fluid mixture was achieved with a heating mantle while a magnetic stirrer was used to mix the contents of the boiling flask. The temperature outside the equilibrium chamber was maintained approximately 1 K lower than the equilibrium temperature by means of a thermostated heating jacket.

The temperature was measured by a thermometer calibrated by the National Bureau of Standards and graduated in increments of 0.2 K. Pressure was measured by a mercury manometer graduated in 0.13 kPa increments. An electronic pressure regulator (constructed by Fischer of West Germany) positioned between the still and a vacuum pump maintained the pressure constant to 0.068 kPa. All experiments were carried out under an inert atmosphere of nitrogen (Matheson Co., purity > 99.99%) to minimize contact with moisture and to accurately control the pressure.

Table I. Physical Properties of Pure Compounds

property	this work	lit.[a]	Δ,[c] %
	m-Xylene		
n_d(293 K)	1.4930	1.4972	0.28
nbp,[d] K	412.1[b]	412.3	0.07
	n-Decane		
n_d(293 K)	1.4080	1.4102	0.16
nbp, K	447.0[b]	447.3	0.06
	Toluene		
n_d(293 K)	1.4904	1.4961	0.38
nbp, K	383.9	383.9	0.01
	Benzene		
n_d(293 K)	1.4960	1.5011	0.34
nbp, K	353.4	353.3	0.01

[a] Literature values taken from ref *12*. [b] Extrapolated from data in 373-393 K range. [c] Δ = 100(measured property − literature property)/(literature property). [d] nbp is the normal boiling point.

Table II. Constants of Eq 1 for Pure Compounds

compd	*A*	*B*	*C*
m-xylene	15.4744	4305.195	−15.437
n-decane	14.8129	3864.601	−65.932
toluene	15.175	3946.675	−9.824

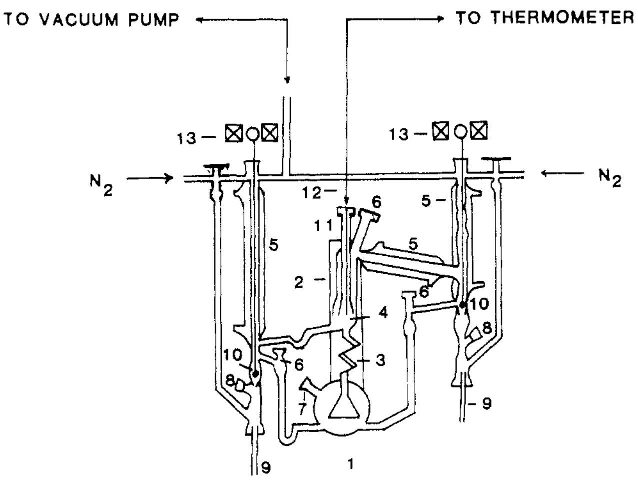

Figure 1. Sketch of Stage-Muller still used in this work: (1) boiling flask, (2) vacuum jacket, (3) Cottrell pump, (4) equilibrium chamber, (5) condensers, (6) injection ports, (7) filling spout and thermometer well, (8) Teflon valves, (9) sample tubes, (10) glass ball valves, (11) equilibrium thermometer well, (12) equilibrium thermometer, (13) solencid devices (actuates 10).

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Table III. Equilibrium Data for the Toluene (1)-*m*-Xylene (2) System

T = 373.6 K			T = 383.6 K			T = 393.7 K		
P, kPa	x	y	P, kPa	x	y	P, kPa	x	y
31.60	0.0	0.0	43.86	0.0	0.0	59.75	0.0	0.0
35.28	0.0756	0.1664	47.70	0.0712	0.1150	64.92	0.0602	0.1106
37.61	0.1300	0.2674	52.84	0.1385	0.2781	75.22	0.1780	0.3427
40.55	0.1947	0.3884	56.00	0.2061	0.3764	84.56	0.2960	0.4981
45.39	0.3026	0.5123	62.16	0.3157	0.5121	93.75	0.4306	0.6320
46.93	0.3279	0.5503	68.80	0.4383	0.6385	99.89	0.5051	0.7009
48.27	0.3707	0.5959	76.22	0.5558	0.7524	106.14	0.5953	0.7589
50.12	0.4148	0.6379	83.57	0.6988	0.8393	114.37	0.6952	0.8422
51.82	0.4569	0.6720	90.89	0.8073	0.9087	122.32	0.7982	0.9087
53.63	0.4975	0.7069	98.54	0.9289	0.9690	128.25	0.8945	0.9467
55.95	0.5404	0.7449	101.07	1.0	1.0	133.15	1.0	1.0
57.27	0.5936	0.7841						
61.34	0.6672	0.8333						
66.11	0.7859	0.9004						
68.73	0.8457	0.9278						
71.20	0.8945	0.9545						
75.56	1.0	1.0						

Table IV. Equilibrium Data for the Toluene (1)-*n*-Decane (2) System

T = 373.5 K			T = 383.6 K			T = 393.7 K		
P, kPa	x	y	P, kPa	x	y	P, kPa	x	y
9.45	0.0	0.0	14.10	0.0	0.0	20.45	0.0	0.0
11.63	0.0353	0.2415	17.78	0.0472	0.2595	26.69	0.0607	0.2854
14.18	0.0700	0.3834	24.20	0.1070	0.4727	44.87	0.1351	0.5109
17.24	0.1223	0.5147	28.91	0.1533	0.5891	57.26	0.2115	0.6441
22.71	0.1880	0.6544	38.24	0.2416	0.7204	68.02	0.3174	0.7555
29.53	0.3006	0.7732	45.90	0.3294	0.7910	81.40	0.4039	0.8178
34.26	0.3665	0.8277	59.86	0.4483	0.8604	93.27	0.5408	0.8896
45.24	0.5301	0.9029	66.44	0.5841	0.9056	102.51	0.6475	0.9196
50.04	0.6144	0.9251	75.67	0.6897	0.9362	111.33	0.8242	0.9618
58.68	0.7769	0.9560	90.17	0.8538	0.9704	127.11	0.9570	0.9874
66.37	0.8617	0.9746	100.99	1.0	1.0	133.12	1.0	1.0
75.38	1.0	1.0						

Table V. Equilibrium Data for the *m*-Xylene (1)-*n*-Decane (2) System

T = 373.5 K			T = 383.6 K			T = 393.7 K		
P, kPa	x	y	P, kPa	x	y	P, kPa	x	y
9.56	0.0	0.0	14.30	0.0	0.0	20.91	0.0	0.0
10.26	0.0286	0.1932	15.43	0.0723	0.1188	22.37	0.0382	0.1060
11.41	0.0854	0.2608	17.26	0.1118	0.2670	25.50	0.1001	0.2662
14.54	0.1835	0.4688	19.99	0.1788	0.4228	30.47	0.1991	0.4551
16.87	0.2929	0.6017	23.43	0.2887	0.5652	35.69	0.3288	0.6019
20.08	0.4429	0.7166	26.83	0.3958	0.6677	41.07	0.4587	0.7150
23.52	0.6122	0.8042	30.15	0.5316	0.7625	46.16	0.6035	0.8040
25.14	0.7043	0.8631	34.21	0.6727	0.8402	51.27	0.7246	0.8668
28.10	0.8158	0.9210	36.36	0.7373	0.8750	56.43	0.8670	0.9384
30.41	0.9197	0.9676	40.41	0.8734	0.9410	60.87	1.0	1.0
31.80	1.0	1.0	42.64	0.9245	0.9723			
			44.42	1.0	1.0			

The compositions of the liquid and condensed vapor samples were determined by a gas chromatograph (Hewlett-Packard, Model 5790A) with a thermal conductivity detector. The chromatographic peaks were analyzed with an electronic integrator (Hewlett-Packard, Model 3390A). A stainless-steel column packed with 2% OV-101 on 100/120 mesh Chromosorb W-HP packing was used. Temperature programming was employed with an initial temperature of 323 K, a ramp of 7.5 K/min, and a final temperature of 448 K. An internal standard was employed and each sample was analyzed at least twice. The accuracy of this method was found to be better than 0.2 mol %.

Steady-state conditions, signified by stable temperature and pressure readings, usually required approximately 60 min for each data point.

All chemicals used in this work had a minimum stated purity from the manufacturer (Alfa and Fisher) of at least 99+ mol %. Each sample was tested on the gas chromatograph described above for any secondary peaks. No secondary peaks were observed. Physical property measurements (Table I) also proved satisfactory and the chemicals were used without further purification. Pure-component vapor pressures were measured by using the recirculating still and were correlated by using the Antoine equation:

$$\ln P = A - B/(T + C) \tag{1}$$

The constants are tabulated in Table II and pure-component vapor pressures at the temperatures of interest are included in Tables III-V.

Results and Discussion

The experimental P-T-x-y data for the three binary systems studied are given in Tables III-V. No data could be found in

Table VI. Best-Fit Parameters and Deviations

	van Laar				UNIQUAC				Margules				Wilson			
T, K	A_{12}	A_{21}	ΔP, kPa	Δy	A_{12}	A_{21}	ΔP, kPa	Δy	A_{12}	A_{21}	ΔP, kPa	Δy	A_{12}	A_{21}	ΔP, kPa	Δy
							Toluene (1)–*m*-Xylene (2)									
373.6	0.02	0.05	0.12	0.0066	119.05	-98.13	0.12	0.0064	-0.01	-0.08	0.13	0.0052	-202.29	309.44	0.12	0.0064
383.6	0.03	0.32	0.21	0.0044	151.97	-122.23	0.18	0.0046	0.04	0.07	0.23	0.0043	-269.96	423.90	0.19	0.0046
393.7	0.06	0.5	0.17	0.0061	271.82	-186.69	0.21	0.0065	0.18	0.24	0.16	0.0113	-397.68	834.54	0.21	0.0064
							Toluene (1)–*n*-Decane (2)									
373.5	0.07	0.06	0.19	0.0036	-148.03	201.45	0.20	0.0038	0.05	0.04	0.19	0.0036	583.98	-529.35	0.19	0.0036
383.6	0.17	0.34	0.27	0.0039	-142.0	176.0	0.27	0.0039	0.08	-0.17	0.27	0.0044	154.85	171.24	0.27	0.0039
393.7	0.06	0.07	0.14	0.0057	-140.16	188.02	0.14	0.0059	0.01	-0.08	0.14	0.0058	438.26	-375.26	0.15	0.0057
							m-Xylene (1)–*n*-Decane (2)									
373.8	0.35	0.14	0.32	0.0094	-210.9	318.72	0.31	0.0092	0.29	0.53	0.22	0.0075	1092.73	-715.55	0.31	0.0095
383.6	0.03	0.03	0.21	0.0096	-124.12	150.07	0.21	0.0095	-0.85	-0.70	0.25	0.0080	293.05	-266.9	0.21	0.0096
393.7	0.14	0.21	0.13	0.0042	-70.51	92.42	0.13	0.0042	-0.90	-0.95	0.18	0.0039	172.35	13.56	0.13	0.0042

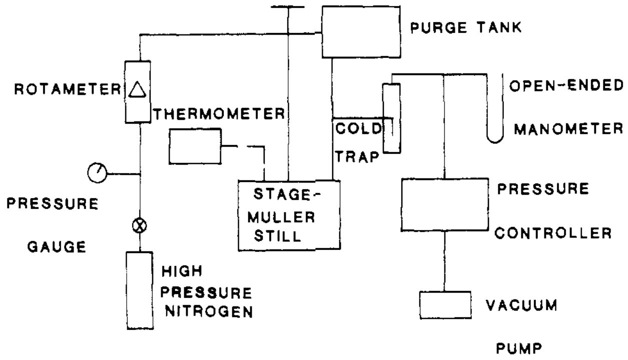

Figure 2. Overall sketch of experimental setup.

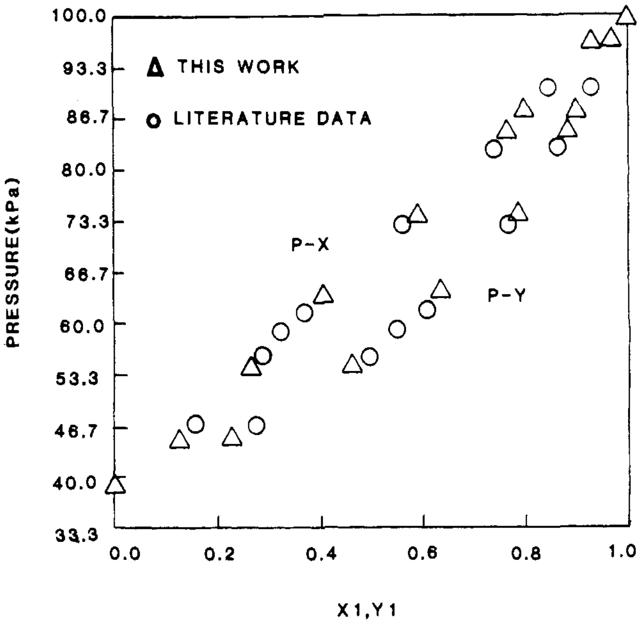

Figure 3. P–x–y phase equilibrium diagram for the benzene (1)–toluene (2) system at 352.8 K.

the literature for any of the systems studied. Binary P–T–x–y data for the benzene + toluene system at 352.8 K were therefore also measured for comparison. These data agreed well with those of Beatty and Callingaert (*2*) and are shown in Figure 3. A P–x–y phase equilibrium diagram for the *m*-xylene (1)–*n*-decane system at 373.8, 384, and 394.3 K is given in Figure 4.

The thermodynamic consistency of the data was examined by using the point-to-point test originated by van Ness et al. (*3*) and modified by Fredenslund et al. (*4*). According to this test, a data point is considered consistent if the average absolute deviation in $\Delta y \leq 0.01$. All points reported in Tables III–VI satisfy this criterion.

Activity Coefficient Correlations

Activity coefficients γ_i at each data point were calculated by using

$$\gamma_i = (\hat{\phi}_i y_i P)/\{x_i P_i^s \phi_i^s \exp((v_i^L/RT)(P - P_i^s))\} \qquad (2)$$

where x_i, y_i are the liquid and vapor mole fractions, ϕ_i is the fugacity coefficient, v_i^L is the pure-liquid molar volume, P is the pressure, and the superscript s refers to a saturation property. The fugacity coefficients were calculated by using the virial equation truncated after the second term:

$$\ln \hat{\phi}_i = (P/RT)\{2 \sum_{j=1}^{N} y_j B_{ij} - B\} \qquad (3)$$

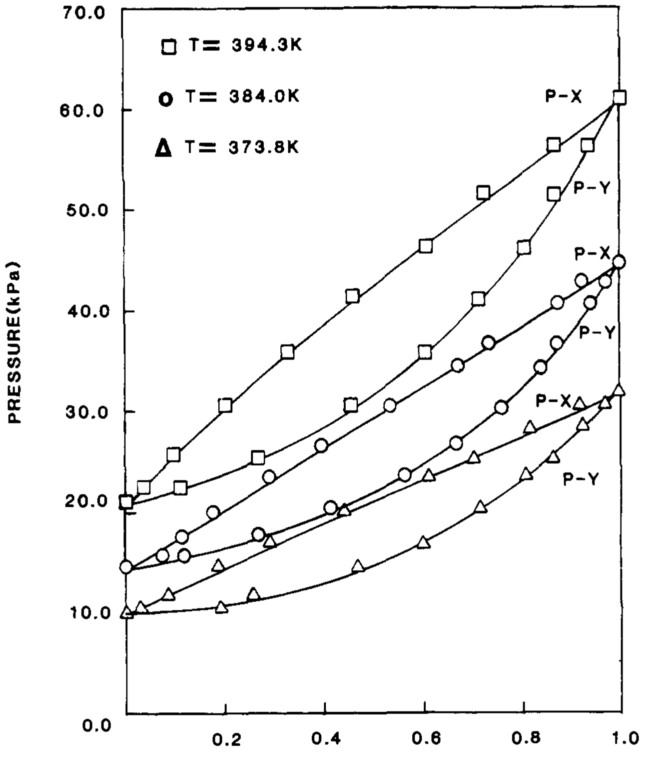

Figure 4. P-x-y phase equilibrium diagram for the *m*-xylene (1)-*n*-decane system at 373.8, 384, and 394.3 K.

The second virial coefficients B were obtained by using the method of Hayden and O'Connell (*5*). The liquid molar volumes v_i^L in eq 2 were assumed to be independent of pressure and were calculated by using the modified Rackett (*6*) equation.

The activity coefficients for each system were then correlated by using the van Laar (*7*), three-suffix Margules (*8*), Wilson (*9*), and UNIQUAC (*10*) models. The two adjustable parameters for each model were estimated by minimizing the function

$$S = \sum_{k=1}^{N} \frac{(P_{k,\mathrm{calcd}} - P_{k,\mathrm{exptl}})^2}{{\sigma_{Pk}}^2} + \sum_{k=1}^{N} \frac{(T_{k,\mathrm{calcd}} - T_{k,\mathrm{exptl}})^2}{{\sigma_{Tk}}^2} + \sum_{k=1}^{N} \frac{(x_{1,\mathrm{calcd}} - x_{1,\mathrm{exptl}})^2}{{\sigma_{Pk}}^2} + \sum_{k=1}^{N} \frac{(y_{1,\mathrm{calcd}} - y_{1,\mathrm{exptl}})^2}{{\sigma_{yk}}^2} \quad (4)$$

using the maximum likelihood method (*11*). The variances in eq 4 represent the estimated errors in each of the measured quantities (P, T, x, and y). The values used in this work of $\sigma_P = 0.17$ kPa, $\sigma_T = 0.07$ K, $\sigma_x = 0.003$, and $\sigma_y = 0.005$ are consistent with the accuracy of the equipment used.

The results of the parameter estimation appear in Table VI. A lower value of the AAD(Δy) and AAD(ΔP) is indicative of a better fit of the data by a particular model. As expected, however, there is little difference between any of the liquid-phase models for the systems studied.

Glossary

A, B, C	constants in the Antoine equation
B	second virial coefficient
i, j	component i, j
L	liquid phase
n	number of components
P	pressure
R	gas constant
T	temperature
v	molar volume
x	liquid-phase mole fraction
y	vapor-phase mole fraction
γ	activity coefficient
σ	standard deviation
ϕ	fugacity coefficient (circumflex indicates value in a mixture)
AAD	average absolute deviation = $(1/N)\sum$[(calculated value - experimental value)/experimental value]
RMSD	root mean square deviation = $\{[1/(N - 3)]\sum(\text{calculated value - experimental value})^2\}^{1/2}$

Registry No. Toluene, 108-88-3; *m*-xylene, 108-38-3; decane, 124-18-5.

Literature Cited

(1) Gutsche, B.; Knapp, H. *Fluid Phase Equilib*. **1982**, *8*, 285.
(2) Beatty, H. A.; Callingaert, G. *Ind. Eng. Chem*. **1934**, *26*, 504.
(3) van Ness, H. C.; Byer, S. M.; Gibbs, R. E. *AIChE J*. **1973**, *19*, 238.
(4) Fredenslund, Ag.; Gmehling, J.; Rasmussen, P. "Vapor-Liquid Equilibria Using UNIFAC"; Elsevier: Amsterdam, 1977.
(5) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev*. **1975**, *14*, 209.
(6) Spencer, C. F.; Danner, R. P. *J. Chem. Eng. Data* **1972**, *17*, 236.
(7) van Laar, J. J. *Z. Phys. Chem*. **1910**, *72*, 723.
(8) Margules, M. *S. B. Akad. Wiss. Wien. Math Naturv*. **1895**, *104*, 243.
(9) Wilson, G. M. *J. Am. Chem. Soc*. **1964**, *86*, 127.
(10) Abrams, D. S.; Prausnitz, J. M. *AIChE J*. **1975**, *21*, 116.
(11) Anderson, T. F.; Abrams, D. S.; Grens, E. A. *AIChE J*. **1978**, *24*, 20.
(12) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 57th ed.; CRC Press: Boca Raton, FL, 1977.

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