

Vapor-Liquid Equilibria for the Binary Systems of Benzene/Toluene, Diphenylmethane/Toluene, *m*-Cresol/1,2,3,4-Tetrahydronaphthalene, and Quinoline/Benzene

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Vapor-liquid equilibrium (VLE) data for the binary systems of benzene/toluene, diphenylmethane/toluene, *m*-cresol/1,2,3,4-tetrahydronaphthalene, and benzene/quinoline were measured at low to moderate pressures (0-1733 kPa) by using a static equilibrium cell. The data were isothermally correlated by using the Peng-Robinson equation of state to describe both vapor and liquid phases. The data were also correlated by using the Peng-Robinson equation of state to describe the vapor phase and the universal quasi-chemical (UNIQUAC) excess Gibbs free energy expression for the liquid phase. Interaction parameters for both the Peng-Robinson and the UNIQUAC equations are reported at each isotherm.

Introduction

For coal liquid mixtures, many components are high molecular weight aromatics and binary data for systems containing such compounds are relatively scarce. Isothermal VLE data are presented for the following systems which can be considered as model compounds for coal liquids: benzene/toluene, diphenylmethane/toluene, *m*-cresol/1,2,3,4-tetrahydronaphthalene, and benzene/quinoline. The data were isothermally regressed by using the Peng-Robinson (1) equation of state to model both vapor and liquid phases, and by using the Peng-Robinson equation to model the vapor phase and the universal quasi-chemical (UNIQUAC) (2) excess Gibbs free energy expression to model the liquid phase. It is our goal to present binary interaction parameters for the Peng-Robinson equation of state and UNIQUAC expression which will be useful in predicting the phase behavior of the coal liquids.

Experimental Section

A schematic diagram of the apparatus can be found in Figure 1. The static equilibrium cell consists of a stainless steel vessel with a volume of approximately 70 mL. Temperature is controlled by a Tecam fluidized temperature regulating sandbath and temperature controller (298-623 K). At the beginning of an experiment, the equilibrium vessel was charged with 50 mL (liquid) of a pure or binary mixture. If a mixture was used, it was stirred thoroughly before charging it to the vessel and no further internal stirring was necessary. Equilibrium conditions were assumed when constant temperature and constant pressure readings were obtained for a period of 15 min or longer and the pressure readings at such conditions were taken as equilibrium bubble pressures for the charged fluid. Both the vapor-phase and liquid-phase temperatures were monitored at all times. The vapor-phase temperature, which was always slightly (1 °C) lower than the liquid-phase temperature, was used as the experimental value because the equilibrium vapor pressures agreed more closely with the literature values when this temperature was used.

All temperatures throughout the apparatus were measured by using stainless steel sheath Carboy Type K thermocouples. The thermocouples were calibrated with a high precision mercury thermometer with an accuracy of ± 0.05 °C.

Table I. Pure Component Data

	temp, K	vap press., kPa
$A1^a = 15.1413, B1 = 5078.0, C1 = 53.89, \Delta P_{err}^b = 0.066$		
diphenylmethane	457.95	13.10
	488.05	31.00
	527.35	82.72
	560.95	168.9
	581.85	250.2
$A1^a = 14.3430, B1 = 4062.0, C1 = 62.44, \Delta P_{err}^b = 0.061$		
1,2,3,4-tetrahydronaphthalene	450.55	48.25
	464.55	69.62
	489.25	124.9
	508.25	186.8
	527.45	272.3
	543.85	367.4
	562.25	501.1
	582.25	684.5
$A1^a = 15.5337, B1 = 4594.0, C1 = 54.34, \Delta P_{err}^b = 0.068$		
<i>m</i> -cresol	466.35	79.96
	472.95	95.54
	493.75	160.6
	510.85	237.9
	531.35	366.2
	565.45	695.5
	588.65	1028.5
$A1^a = 14.4961, B1 = 4390.0, C1 = 65.19, \Delta P_{err}^b = 0.102$		
quinoline	472.85	42.12
	504.95	90.99
	514.35	112.4
	534.35	170.3
	548.05	222.6

$$^a \log P \text{ (kPa)} = A1 - B1/(T \text{ (kelvin)} + C1). \quad ^b \Delta P_{err} = [\sum_{i=1}^N (P_{exptl} - P_{calcd})^2 / N]$$

Pressure measurements were monitored with two Viatran pressure transmitters. Low-pressure measurements were made with a Viatran, Model 501-115, 0-173 kPa transmitter. Pressure readings greater than 173 kPa were measured with a Viatran Model 501-115, 0-1733 kPa transmitter. Both transmitters were calibrated to $\pm 0.25\%$ of the full-scale pressure.

The following list of chemicals were available with a purity of 99 mol % or greater. Benzene was obtained from Fischer Scientific (B-414). Toluene was available as a Baker Analyzed Reagent. Aldrich supplied the remaining chemicals of 1,2,3,4-tetrahydronaphthalene (10,241-5), quinoline (24,157-1), diphenylmethane (24,007-9), and *m*-cresol (24,007-9). As a secondary measure, the components were analyzed by using a gas chromatograph showing the dominant peak to have an area of no less than 99% of the total. All chemicals were used with no further purification.

Results and Conclusions

Due to the high sensitivity of vapor pressure to chemical purity and experimental conditions, the vapor pressures of the pure components were measured with the same apparatus and from the same chemical batch as those for the binary mixtures (8). The pure component vapor pressure data obtained are

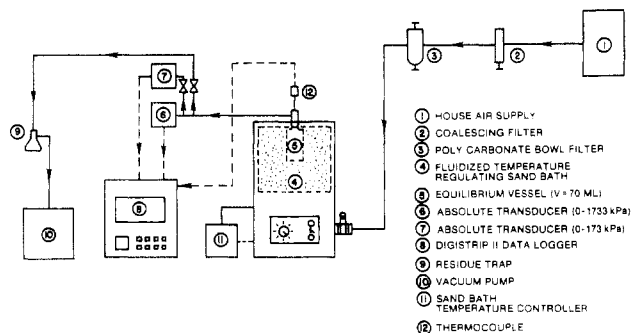


Figure 1. Experimental apparatus.

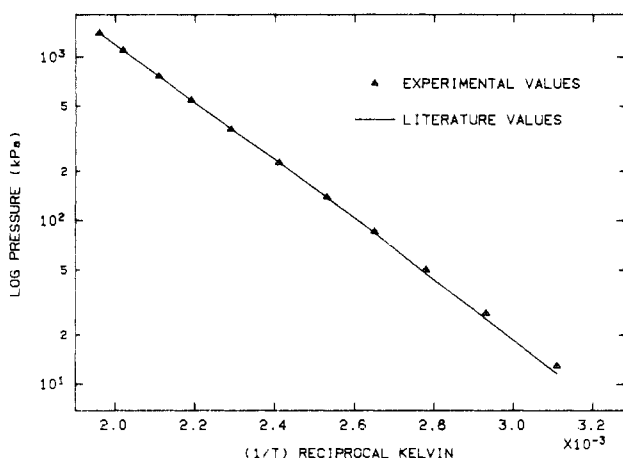


Figure 2. log pressure (kPa) vs. reciprocal kelvin for pure toluene.

presented in Table I. The data were also correlated by using the Antoine equation

$$\log P = A - B/(T + C) \quad (1)$$

where pressure is in kilopascals and temperature in kelvin. The constants (A , B , C) were determined by using a least-squares technique and an external penalty method for locating the optimal region. The Antoine constants are listed in Table I.

The accuracy of the data obtained by using the above experimental equipment and procedure was determined through a comparison with Antoine equations and literature data for pure component systems (3–5) and literature data for the binary system of benzene/toluene at 373.15 and 393.15 K (6, 7). For pure component systems the average error between the literature data and the Antoine equations obtained with our results is 3 kPa and the maximum error is 7 kPa. As illustrated in Figure 2, the error is a larger percentage of the measured pressure in the low-pressure range. Here the literature values are represented by an Antoine equation (3) because it reproduces the experimental literature data (4, 5) with an average error of 1 kPa which is only a third of the error we report. For the binary system the average errors are given in Table II. The maximum percent deviation from the literature pressures is $\pm 2\%$ with the average deviation being less than 1%.

The P - x - T data are regressed by using the Peng–Robinson equation to describe both phases. Subsequently the Peng–Robinson equation was used only for the vapor phase while the universal quasi-chemical (UNIQUAC) Gibbs free energy expression was employed to calculate the activity coefficient in the liquid phase. The interaction parameters in both the Peng–Robinson and UNIQUAC expressions are obtained when the objective function

$$\sum_{i=1}^n (P_{\text{exptl}} - P_{\text{calcd}}) / P_{\text{exptl}} / N$$

was found to be minimum.

Table II. Literature Comparison of the Benzene/Toluene System (6)

temp, K	$P_{\text{lit.}}^a$ kPa	P_{exptl} kPa	ΔP , kPa
$x(\text{Benzene}) = 0.226$			
373.15	100.7	101.1	0.4
393.15	165.3	164.2	-1.1
$x(\text{Benzene}) = 0.566$			
373.15	137.9	136.7	-1.2
393.15	228.1	227.1	-1.0
$x(\text{Benzene}) = 0.793$			
373.15	159.9	156.6	-3.3
393.15	265.7	262.6	-3.1

^a Literature data are interpolated over composition with an average accuracy of 0.5 kPa.

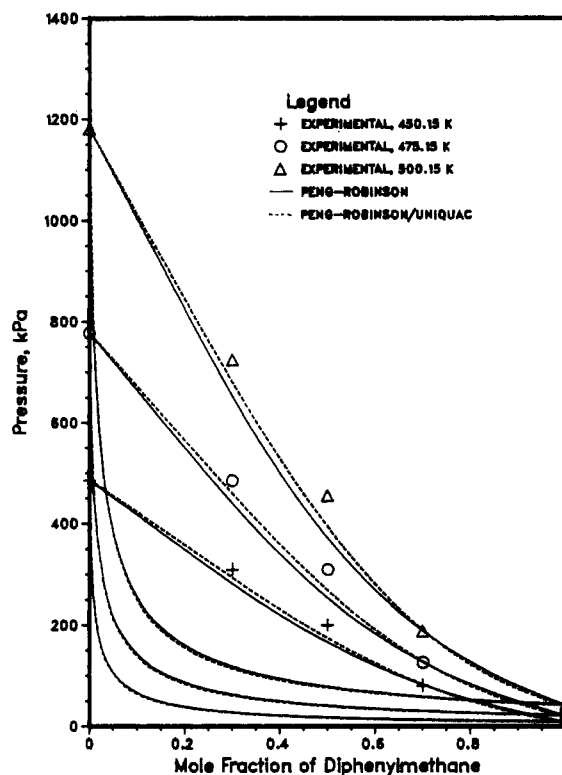


Figure 3. Equilibrium pressure vs. composition diagram for the diphenylmethane/toluene system.

A comparison of experimental to predicted pressures is shown in Tables III–VI. This is also illustrated in Figure 3 for the diphenylmethane (1)/toluene (2) system. The differences between predicted and calculated results are small, and are primarily due to the limitations in the accuracy of the experimental data. The calculated results represent the optimum correlation of the data obtained with the associated binary interaction parameters.

Glossary

A , B , C	Antoine constants
A	constant (eq 3)
a	attraction parameter
a_{ij}	UNIQUAC binary interaction parameter related to ΔU_{ij} and τ_{ij} ($a_{ij} = \Delta U_{ij}/R$)
B	constant (eq 4)
b	van der Waals covolume, m^3
I_i	pure component constant defined by eq 12
N	number of experimental data points
P	total system pressure, kPa

Table III. Vapor-Liquid Equilibrium Data for Benzene (1)/Toluene (2) at 325.15, 373.15, and 410.15 K

exptl values		predicted values					
x_1	P , kPa	Peng-Robinson		Peng-Robinson/UNIQUAC			
		y_1	P , kPa	y_1	P , kPa	γ_1	γ_2
$T = 325.15$ K							
0	13.4 ^a	0	13.4	0	13.4	0.955	1.0
0.226	19.9	0.478	19.9	0.477	19.8	0.959	0.999
0.306	21.8	0.583	22.2	0.581	22.2	0.963	0.997
0.566	32.6	0.810	30.2	0.809	30.1	0.982	0.982
0.793	36.0	0.928	37.5	0.929	37.4	0.995	0.954
1.0	44.1	1.0	44.1	1.0	44.1	1.0	0.914
av error, ^b Y		0.2228×10^{-1}		0.2224×10^{-1}			
$T = 373.15$ K							
0	75.8	0	75.8	0	75.8	0.783	1.0
0.226	92.5	0.377	93.9	0.378	93.8	0.866	0.987
0.306	101.4	0.486	101.4	0.488	101.4	0.891	0.977
0.566	138.1	0.759	129.5	0.761	130.1	0.956	0.925
0.793	157.7	0.912	158.2	0.912	158.7	0.990	0.860
1.0	185.8	1.0	185.8	1.0	185.8	1.0	0.789
av error, ^b Y		0.1342×10^{-1}		0.1299×10^{-1}			
$T = 410.15$ K							
0	201.9	0	201.9	0	201.9	0.773	1.0
0.226	236.8	0.346	239.4	0.347	239.0	0.860	0.986
0.306	255.4	0.453	255.4	0.455	255.4	0.887	0.972
0.566	329.8	0.734	317.3	0.737	318.9	0.955	0.922
0.793	385.9	0.902	382.8	0.901	384.2	0.990	0.855
1.0	447.7	1.0	447.7	1.0	447.7	1.0	0.782
av error, ^b Y		0.95×10^{-2}		0.7847×10^{-2}			
Interaction Parameters							
T , K		Peng-Robinson δ_{12}		UNIQUAC			
				a_{12} , K		a_{21} , K	
325.15		-0.004 727		-146.0		180.7	
373.15		-0.020 50		-168.8		178.5	
410.15		-0.025 55		-168.9		168.5	

^aLiterature data (3). ^bAverage error, $Y = (\sum_{i=1}^N |(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}|)/N$.

Table IV. Vapor-Liquid Equilibrium Data for Diphenylmethane (1)/Toluene (2) at 450.15, 475.15, and 500.15 K

exptl values		predicted values					
x_1	P , kPa	Peng-Robinson		Peng-Robinson/UNIQUAC			
		y_1	P , kPa	y_1	P , kPa	γ_1	γ_2
$T = 450.15$ K							
0	485.4	0	485.4	0	485.4	0.316	1.0
0.3	309.2	0.007	280.1	0.006	294.0	0.563	0.903
0.5	199.9	0.024	162.2	0.021	172.2	0.741	0.752
0.7	80.3	0.076	80.3	0.073	80.3	0.894	0.566
1.0	8.9 ^a	1.0	8.9	1.0	8.9	1.0	0.298
av error, ^b Y		0.5633×10^{-1}		0.3753×10^{-1}			
$T = 475.15$ K							
0	776.6	0	776.6	0	776.6	0.304	1.0
0.3	484.6	0.011	437.9	0.010	459.5	0.551	0.900
0.5	308.5	0.039	251.1	0.034	266.6	0.733	0.744
0.7	126.0	0.119	126.0	0.114	126.0	0.891	0.555
1.0	21.6	1.0	21.6	1.0	21.6	1.0	0.285
av error, ^b Y		0.5649×10^{-1}		0.3753×10^{-1}			
$T = 500.15$ K							
0	1181.5	0	1181.5	0	1181.5	0.303	1.0
0.3	724.5	0.016	650.4	0.015	679.9	0.548	0.900
0.5	455.7	0.054	370.6	0.048	392.6	0.729	0.744
0.7	188.9	0.159	188.9	0.152	188.9	0.888	0.553
1.0	42.7	1.0	42.7	1.0	42.7	1.0	0.278
av error, ^b Y		0.5783×10^{-1}		0.4002×10^{-1}			
Interaction Parameters							
T , K		Peng-Robinson δ_{12}		UNIQUAC			
				a_{12} , K		a_{21} , K	
450.15		-0.09697		390.9		-365.1	
475.15		-0.1141		451.4		-405.2	
500.15		-0.1303		416.0		-402.5	

^aLiterature data (3). ^bAverage error, $Y = (\sum_{i=1}^N |(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}|)/N$.

Table V. Vapor-Liquid Equilibrium Data for *m*-Cresol (1)/1,2,3,4-Tetrahydronaphthalene (2) at 450.15, 500.15, and 550.15 K

exptl values		predicted values					
x_1	P , kPa	Peng-Robinson		Peng-Robinson/UNIQUAC			
x_1	P , kPa	y_1	P , kPa	y_1	P , kPa	γ_1	γ_2
$T = 450.15$ K							
0	47.8	0	47.8	0	47.8	1.669	1.0
0.3	50.9	0.377	56.5	0.378	55.9	1.388	1.036
0.5	59.9	0.526	58.5	0.535	58.1	1.226	1.127
0.7	58.2	0.660	58.2	0.669	58.2	1.096	1.339
0.9	54.1	0.841	54.8	0.839	55.1	1.013	1.856
1.0	50.6	1.0	50.6	1.0	50.6	1.0	2.399
av error, ^a Y		0.2433×10^{-1}		0.2427×10^{-1}			
$T = 500.15$ K							
0	158.1	0	158.1	0	158.1	1.480	1.0
0.3	166.6	0.383	187.5	0.385	186.5	1.284	1.027
0.5	196.9	0.548	196.9	0.554	196.8	1.168	1.096
0.7	200.5	0.696	199.7	0.700	200.5	1.072	1.250
0.9	194.3	0.872	194.4	0.869	195.5	1.010	1.600
1.0	186.6	1.0	186.6	1.0	186.6	1.0	1.940
av error, ^a Y		0.2163×10^{-1}		0.2099×10^{-1}			
$T = 550.15$ K							
0	409.3	0	409.3	0	409.3	1.281	1.0
0.3	475.4	0.379	481.2	0.380	479.7	1.169	1.017
0.5	511.8	0.560	511.8	0.564	511.8	1.101	1.060
0.7	532.2	0.723	529.6	0.725	531.1	1.043	1.151
0.9	533.6	0.896	533.2	0.894	534.7	1.006	1.338
1.0	527.5	1.0	527.5	1.0	527.5	1.0	1.501
av error, ^b Y		0.2995×10^{-2}		0.2243×10^{-2}			

Interaction Parameters

T , K	Peng-Robinson δ_{12}	UNIQUAC	
		a_{12} , K	a_{21} , K
450.15	0.039 38	191.4	-83.50
500.15	0.037 38	190.8	-96.64
550.15	0.029 63	171.2	-103.5

^a Average error, $Y = (\sum_{i=1}^N |(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}|)/N$.

Table VI. Vapor-Liquid Equilibrium Data for Benzene (1)/Quinoline (2) at 350.15, 400.15, and 450.15 K

exptl values		predicted values					
x_1	P , kPa	Peng-Robinson		Peng-Robinson/UNIQUAC			
x_1	P , kPa	y_1	P , kPa	y_1	P , kPa	γ_1	γ_2
$T = 350.15$ K							
0	0.4 ^a	0	0.4	0	0.4	0.282	1.0
0.3	16.1	0.984	16.1	0.985	16.1	0.553	0.890
0.5	44.0	0.995	33.5	0.996	35.9	0.745	0.729
0.7	69.0	0.999	57.7	0.999	61.2	0.902	0.548
1.0	97.9	1.0	97.9	1.0	97.9	1.0	0.308
av error, ^b Y		0.8080×10^{-1}		0.5968×10^{-1}			
$T = 400.15$ K							
0	3.7 ^a	0	3.7	0	3.7	0.309	1.0
0.3	59.0	0.957	59.0	0.959	59.0	0.565	0.899
0.5	153.3	0.987	121.3	0.988	128.5	0.748	0.746
0.7	244.4	0.996	209.3	0.997	219.5	0.901	0.564
1.0	358.7	1.0	358.7	1.0	358.7	1.0	0.313
av error, ^b Y		0.7052×10^{-1}		0.5284×10^{-1}			
$T = 450.15$ K							
0	22.9	0	22.9	0	22.9	0.332	1.0
0.3	162.8	0.901	162.8	0.904	162.8	0.582	0.906
0.5	403.6	0.967	324.6	0.970	340.1	0.758	0.760
0.7	651.7	0.990	560.3	0.991	581.6	0.905	0.583
1.0	983.5	1.0	983.5	1.0	983.5	1.0	0.330
av error, ^b Y		0.6722×10^{-1}		0.5295×10^{-1}			

Interaction Parameters

T , K	Peng-Robinson δ_{12}	UNIQUAC	
		a_{12} , K	a_{21} , K
350.15	-0.070 38	-179.7	45.71
400.15	-0.086 90	-181.0	27.73
450.15	-0.106 70	-191.6	26.40

^a Literature data (9). ^b Average error, $Y = (\sum_{i=1}^N |(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}|)/N$.

P_{calcd}	calculated total system pressure, kPa
P_{exptl}	experimental total system pressure, kPa
q_i	molecular-geometric area parameter for component i
q'_i	molecular interaction area parameter for component i
R	gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
r_i	molecular volume parameter for pure component i
T	system temperature, K
T_r	reduced temperature
ΔU_{ij}	UNIQUAC binary interaction parameter
v	molar volume, $\text{m}^3/(\text{kg mol})$
x	liquid mole fraction
x_i	mole fraction of component i
y	vapor mole fraction
z	lattice coordination number, here equal to 10
Z	compressibility factor
γ_i	activity coefficient of component i
δ_{ij}	binary interaction parameter
Θ_i	area fraction of component i in combinatorial contribution to the activity coefficient
Θ'_i	area fraction of component i in residual contribution to the activity coefficient
κ	characteristic constant
τ_{ij}	UNIQUAC binary parameter
ϕ_i	segment fraction of component i

Appendix

The Peng–Robinson (1) equation of state was used to regress all the binary experimental data. This equation can be written in cubic form as follows

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (2)$$

where

$$A = \frac{aP}{R^2T^2} \quad (3)$$

$$B = \frac{bP}{RT} \quad (4)$$

$$Z = \frac{Pv}{RT} \quad (5)$$

The mixing rules are defined by

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

$$b = \sum_i x_i b_i \quad (7)$$

$$a_{ij} = (1 - \delta_{ij})a_i^{1/2}a_j^{1/2} \quad (8)$$

where the constant δ_{ij} is designated the binary interaction pa-

rameter. This parameter is a slight function of temperature for any given system. The value of δ_{ij} was determined when the objective function

$$\left(\sum_{i=1}^N (P_{\text{exptl}} - P_{\text{calcd}}) / P_{\text{exptl}} \right) / N \quad (9)$$

was found to be a minimum.

The value of a was fitted to the pure component data at each temperature.

The UNIQUAC (2) expression was also used to calculate the liquid-phase activity coefficient model as listed below.

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \left(\frac{z}{2} \right) q_i \ln \frac{\Theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j - q'_i \ln \left(\sum_j \Theta'_j \tau_{ij} \right) + q'_i - q'_i \sum_j \frac{\Theta'_j \tau_{ij}}{\sum_k \Theta'_k \tau_{kj}} \quad (10)$$

$$l_j = \frac{z}{2} (r_j - q_j) - (r_j - 1) \quad (11)$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (12)$$

$$\Theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (13)$$

$$\Theta'_i = \frac{q'_i x_i}{\sum_j q'_j x_j} \quad (14)$$

$$\tau_{ij} = \exp \left(- \frac{a_{ij}}{T} \right) \quad (15)$$

Values of r , q , and q' are obtained from ref 3 and 6.

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