

Vapor-Liquid Equilibria in the Systems Toluene/Naphthalene and Cyclohexane/Naphthalene

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Vapor-liquid equilibrium data for the binary systems toluene/naphthalene and cyclohexane/naphthalene were measured at 0-1300 kPa and 370-500 K using a 1-L stirred autoclave system. All pure components and binary P - T data were well fitted with a three-constant Antoine equation. The data can be accurately correlated with the modified Peng-Robinson equation of state using density-dependent mixing rules to describe both the vapor and liquid phases. The binary interaction parameters and correction factors for the equation of state are reported at each isotherm.

Introduction

Thermodynamic data for many organic systems have been developed for the petroleum industry. Most frequently, these data are for paraffinic systems which are different from the aromatic liquids produced in coal liquefaction. The present study reports further results for vapor-liquid equilibria for model mixtures representing coal-derived liquids. These results contribute to a data base for mixtures containing aromatic compounds which may be present in coal liquefaction processes (1-7).

Vapor pressure measurements of binary mixtures containing compounds which are solid at room temperature are scarce. In this study, we report isothermal vapor-liquid equilibrium (VLE) data for the toluene/naphthalene and cyclohexane/naphthalene systems which can be considered as model compounds for coal liquids. The binary P - x data are isothermally correlated by using the modified Peng-Robinson equation of state (P-R EOS) with density-dependent mixing rules (8, 9) to model both vapor and liquid phases.

Experimental Section

A schematic diagram of the apparatus is shown in Figure 1. Prausnitz et al. (10, 11) indicated that the high melting point of naphthalene made it unsuitable for a recirculating still system from which samples are taken. In this study a closed 1-L constant-temperature cell with temperature and pressure measuring devices was used to determine the vapor-liquid equilibria.

The cell, which is made of 316-stainless steel, was constructed by Autoclave Engineers and equipped with a magnetically driven stirrer, two thermocouple wells, two electric heaters around its periphery, a liquid inlet, a drain line, and a vent/vacuum system. The cell was well-insulated, and the temperature inside the cell was uniform to ± 0.1 K.

The upper heater was controlled by a thermoelectric Eurotherm Model 808 PID controller. The lower heater was independently controlled by a thermoelectric Tecam TC-4D PID controller. The temperatures of the liquid and vapor phases were displayed on a data logger at all times. Two thermocouples (Omega, K-type) were calibrated using a calibrated thermometer (Fischer Scientific, No. 155-041B) with an absolute error of 0.1 K.

The pressure P was measured by a pressure transducer (Setra 205; 0-1724 kPa). The pressure transducer was calibrated to $\pm 0.2\%$ of the full-scale pressure using two calibrated Heise gauges (3447 and 345 kPa, respectively). The transducer line connected to the autoclave system was heated

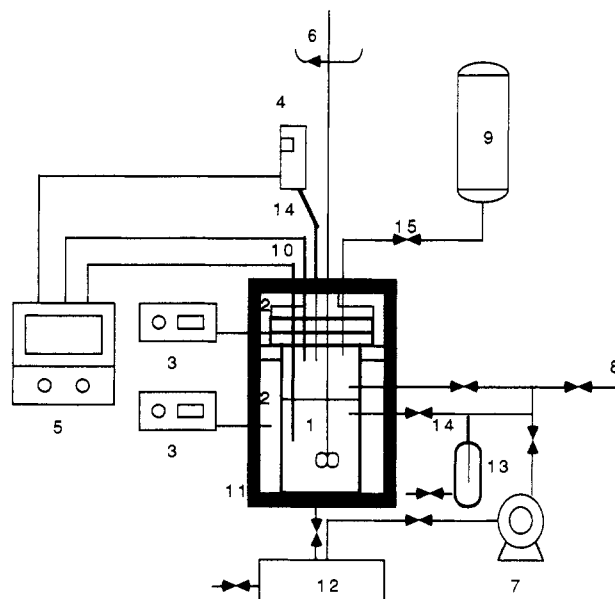


Figure 1. Experimental apparatus: (1) autoclave, (2) heater, (3) temperature controller, (4) pressure transducer, (5) data logger, (6) magnetic stirrer, (7) vacuum pump, (8) vent line, (9) mixture inlet vessel, (10) thermocouple, (11) insulator, (12) drain tank, (13) sampling vessel, (14) heating tape, (15) on-off valve.

to avoid the potential blockage by solid naphthalene. The vessel pressure was recorded on a data logger at 5-min intervals.

A sample of pure or binary liquid was charged to the evacuated stainless steel vessel such that the vapor space was 30% of the vessel volume at room temperature. The pressure exerted by this mixture was then measured as a function of temperature. The composition of the liquid was determined by taking the liquid-phase samples at the lowest experimental temperatures and analyzing them using a gas chromatograph. At each equilibrium temperature, the liquid composition changed (about 0.005 mole fraction on average) due to the vaporization of some of the liquid. Using the Peng-Robinson equation of state, the experimental pressure was corrected by the difference in calculated equilibrium pressures at the two compositions. The maximum correction in pressure was less than 1%. The accuracy of the data was limited by the purity of the liquids (below) and not by this correction. The reported pressures are estimated to be within 2% of the true values at the reported temperature and compositions, with

Table I. Comparison of the Direct Experimental Vapor Pressure P_{exptl} of Pure Toluene, Cyclohexane, and Naphthalene with Values P_{calcd} Calculated Using the Coefficients A , B , and C , for Equation 1, as a Function of Temperature T , and Average Absolute Percent Error, AAPE, Equation 2

T/K	$P_{\text{exptl}}/\text{kPa}$	$P_{\text{calcd}}/\text{kPa}$	
		this work	lit. (12)
Toluene			
331.45	17.44	17.44	17.25
368.30	63.39	63.51	63.69
389.35	116.3	117.5	118.0
397.15	144.7	144.8	145.6
409.25	197.9	196.9	197.8
428.75	308.9	310.0	311.1
429.83	318.4	317.5	318.7
451.25	497.8	496.1	497.0
457.24	556.8	557.5	558.3
472.05	734.3	733.3	733.9
475.86	784.9	784.5	785.2
491.55	1031.5	1023.5	1024.6
496.13	1101.9	1102.3	1104.0
$A = 14.27, B = 3290.24, C = -43.03, \text{AAPE} = 0.30\%$ (this work) $\text{AAPE} = 0.45\%$ (ref 12)			
Cyclohexane			
359.9	118.5	120.3	118.4
381.95	219.1	219.1	219.6
405.22	376.9	376.9	379.9
413.91	454.8	454.4	458.0
428.59	614.7	612.9	616.3
441.62	786.3	786.3	787.8
454.66	987.8	994.6	992.2
469.96	1279.3	1289.5	1279.1
$A = 14.99, B = 3733.11, C = 6.84, \text{AAPE} = 0.42\%$ (this work) $\text{AAPE} = 0.34\%$ (ref 12)			
Naphthalene			
513.05	160.0	160.0	162.1
533.45	236.5	238.2	241.0
553.05	337.2	339.0	341.6
571.45	461.3	460.9	462.6
591.75	632.9	631.5	631.1
612.75	854.3	854.3	850.5
$A = 14.63, B = 4481.67, C = -44.06, \text{AAPE} = 0.27\%$ (this work) $\text{AAPE} = 0.94\%$ (ref 12)			

average errors being less than 1%.

The following list of chemicals were available with a purity of 99% or greater. Aldrich supplied the toluene (No. 27,037-7; 99.9+%), cyclohexane (No. 27,062-8; 99.9+%), and naphthalene (No. 18,450-0; 99+%). The purity was verified using a gas chromatograph (Hewlett-Packard 5880A). All chemicals were used without further purification.

Results

Using an Antoine-type equation (eq 1), all pure components and constant-composition binary P - T data were fitted with an average absolute percent error (AAPE), eq 2, of less than 1%.

$$\ln(P/\text{kPa}) = A - \frac{B}{(T/K) + C} \quad (1)$$

$$\text{AAPE} = \sum_i \frac{|P_{\text{exptl}} - P_{\text{calcd}}|}{P_{\text{exptl}}} \frac{100}{N} \quad (2)$$

The accuracy of the data obtained by using the above experimental equipment and procedure was determined through a comparison with literature data for pure component systems and for the binary system cyclohexane/aniline. Comparison with pure component correlations (12) indicates

Table II. Experimental Bubble Pressure P_{exptl} of the Toluene (1)/Naphthalene (2) System at Mole Fraction x_1 of Toluene as a Function of Temperature T , Coefficients A , B , and C , Equation 1, and Average Absolute Percent Error, AAPE, Equation 2

T/K	$P_{\text{exptl}}/\text{kPa}$	T/K	$P_{\text{exptl}}/\text{kPa}$
$x_1 = 0.2847$		$x_1 = 0.5111$	
382.4	35.40	373.4	46.10
404.7	61.84	394.4	76.10
418.1	85.09	414.3	121.5
435.2	122.7	435.6	194.8
456.5	189.0	435.8	196.6
		455.6	289.7
		478.7	435.0
$A = 14.200, B = 4225.55$		$A = 14.490, B = 4149.08$	
$C = 15.00, \text{AAPE} = 0.30\%$		$C = 14.48, \text{AAPE} = 1.04\%$	
$x_1 = 0.5899$		$x_1 = 0.6724$	
376.3	52.53	373.4	53.95
396.2	87.17	394.9	94.66
406.6	111.1	415.4	158.6
415.8	138.3	434.5	242.6
434.7	207.3	456.1	373.2
435.1	210.5	478.0	549.4
435.7	213.4	502.4	812.0
455.6	320.4		
$A = 14.678, B = 4197.56$		$A = 14.837, B = 4170.22$	
$C = 14.89, \text{AAPE} = 0.56\%$		$C = 10.98, \text{AAPE} = 0.96\%$	
$x_1 = 0.8466$			
375.6	71.80		
395.3	117.5		
413.9	189.6		
436.4	310.0		
457.3	470.1		
478.0	679.0		
$A = 15.017, B = 4140.60$			
$C = 9.77, \text{AAPE} = 0.65\%$			

Table III. Experimental Bubble Pressure P_{exptl} of the Cyclohexane (1)/Naphthalene (2) System at Mole Fraction x_1 of Cyclohexane as a Function of Temperature T , Coefficients A , B , and C , Equation 1, and Average Absolute Percent Error, AAPE, Equation 2

T/K	$P_{\text{exptl}}/\text{kPa}$	T/K	$P_{\text{exptl}}/\text{kPa}$
$x_1 = 0.2727$		$x_1 = 0.3861$	
375.1	71.53	373.2	91.88
395.0	113.1	395.5	154.1
412.8	162.6	414.9	226.5
434.9	242.1	434.5	326.4
457.6	350.8	454.9	454.2
477.0	470.8	477.2	639.7
$A = 13.056, B = 3304.76$		$A = 13.425, B = 3342.50$	
$C = 1.86, \text{AAPE} = 0.46\%$		$C = 2.74, \text{AAPE} = 0.47\%$	
$x_1 = 0.5132$		$x_1 = 0.7933$	
373.4	111.8	372.3	139.7
394.1	182.3	396.8	250.4
415.3	281.4	414.6	364.4
435.5	410.5	434.1	531.6
455.6	576.8	454.4	755.0
476.6	795.0	477.2	1079
$A = 13.754, B = 3373.72$		$A = 14.242, B = 3467.01$	
$C = 0.55, \text{AAPE} = 0.50\%$		$C = 0.80, \text{AAPE} = 0.41\%$	
$x_1 = 0.8879$			
379.9	187.9		
393.8	261.1		
417.3	432.5		
435.8	624.0		
455.3	881.2		
479.8	1306		
$A = 14.576, B = 3559.10$			
$C = 1.16, \text{AAPE} = 0.13\%$			

that experimental errors for pure components were less than 1% (AAPE). For the cyclohexane/aniline binary system (13), the percent deviation from literature pressures was 1.3% (AAPE).

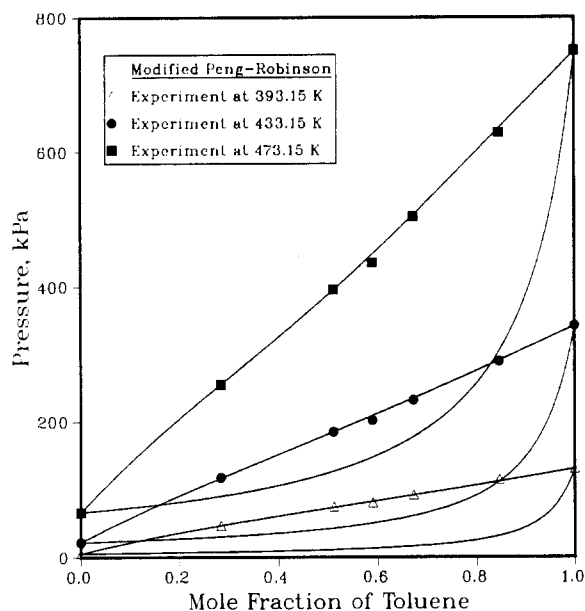


Figure 2. Pressure–equilibrium phase composition diagram for the toluene/naphthalene system.

The vapor pressure measurements of all the systems are shown in Tables I–III. The P - x - T data were correlated to determine the binary interaction parameters for the modified P-R EOS using density-dependent mixing rules (8, 9).

The original P-R EOS (14) is given by

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b) + b(V-b)} \quad (3)$$

where V is the molar volume and R is the gas constant. It contains two adjustable parameters, a and b . a and b are the pure component parameters representing the attractive force between molecules and hard sphere molecular volume, respectively.

The following mixing rules were used for the parameters a and b :

$$b = \sum_i x_i b_i \quad (4)$$

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (5)$$

$$a_{ij} = (a_i a_j)^{1/2} (1 - \delta_{ij}) \quad (6)$$

In the modified version, the interaction parameter δ_{ij} is not a single constant, but varies linearly with the phase molar density of the mixture ($1/V$):

$$\delta_{ij} = \alpha_{ij} + \beta_{ij}/V \quad (7)$$

Using the above mixing rules, the modified P-R EOS can be written as a fourth-order equation in compressibility. The parameters α_{ij} and β_{ij} are adjusted to minimize the error between the calculated and experimental data. For pure components, the original Peng–Robinson equation is obtained since the mixing rules are not used. Details of the modified P-R EOS have been given by Mohamed and Holder (8, 9).

The data can be accurately correlated with the modified P-R EOS as shown in Figures 2 and 3. In this study, the correction factors C_a and C_b were used so that the pure component vapor pressure and liquid molar volumes were accurately predicted. The values of C_a and C_b were obtained from regression of the vapor pressure and liquid molar volume. The modified P-R EOS parameters and correction factors at several temperatures are given in Tables IV and V, and isothermal data at one temperature per system are given in

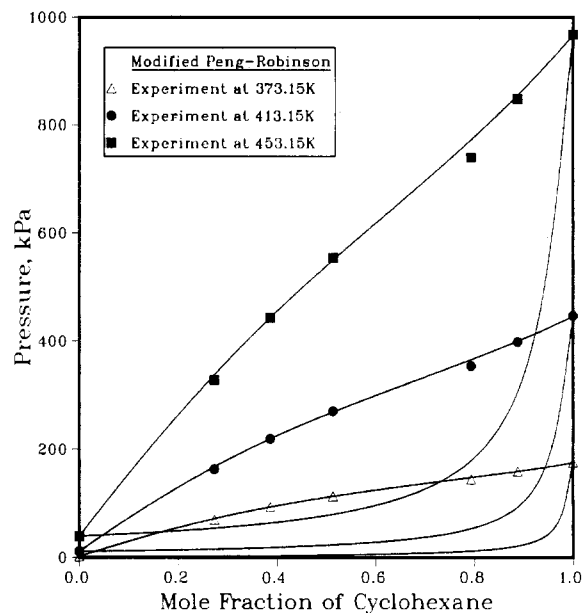


Figure 3. Pressure–equilibrium phase composition diagram for the cyclohexane/naphthalene system.

Table IV. Correction Factors C_a and C_b for the Pure Component Vapor Pressures and Molar Volumes as a Function of Temperature T

T/K	C_a	C_b	T/K	C_a	C_b
Toluene					
373.15	1.0162	1.0041	433.15	1.0104	1.0027
393.15	1.0195	1.0051	453.15	0.9936	0.9990
413.15	1.0185	1.0048	473.15	0.9629	0.9932
Cyclohexane					
373.15	1.1714	1.0479	433.15	1.1577	1.0311
393.15	1.1814	1.0448	453.15	1.1067	1.0196
413.15	1.1789	1.0394	473.15	1.0044	1.0045
Naphthalene					
373.15 ^a	0.9506	0.9742	433.15 ^b	0.9627	0.9838
393.15 ^a	0.9537	0.9776	453.15 ^b	0.9628	0.9857
413.15 ^b	0.9620	0.9810	473.15 ^b	0.9638	0.9874

^a Literature data (15). ^b Literature data (12).

Table V. Interaction Parameters for the Modified Peng–Robinson Equation of State

T/K	$\delta_{12} = \alpha_{12} + \beta_{12}/V$		AAPE
	α_{12}	$\beta_{12}/(\text{cm}^3/\text{mol})$	
Toluene/Naphthalene			
373.15	0.038 75	-5.9029	1.50
393.15	0.065 98	-14.9997	0.89
413.15	0.106 00	-27.8572	0.74
433.15	0.104 75	-29.4924	0.87
453.15	0.148 52	-43.7827	0.81
473.15	0.198 02	-59.6695	0.68
Cyclohexane/Naphthalene			
373.15	-0.242 81	78.1253	0.76
393.15	-0.196 25	65.4738	0.89
413.15	0.163 50	56.4412	1.03
433.15	-0.089 25	34.4602	1.15
453.15	-0.106 90	40.2909	1.30
473.15	-0.079 00	32.0047	1.42

Table VI. The maximum average deviation from the correlation of both systems was 1.5% (AAPE).

Conclusion

Experimental data on binary pairs of aromatics and an aromatic/cyclohexane system are obtained. Such components are representative of those found in coal-derived liquids. The

Table VI. Isothermal Vapor-Liquid Equilibrium Data at 413.15 K

$x_{1,\text{exptl}}$	$y_{1,\text{calcd}}$	$P_{\text{exptl}}/\text{kPa}$	$P_{\text{calcd}}/\text{kPa}$
Toluene (1)/Naphthalene (2)			
0.0	0.0	11.5 ^a	11.5
0.2847	0.8857	76.0	76.0
0.5111	0.9466	120.0	119.3
0.5899	0.9591	130.5	134.3
0.6724	0.9700	149.1	150.2
0.8466	0.9879	186.2	184.9
1.0	1.0	217.1	216.8
Cyclohexane (1)/Naphthalene (2)			
0.0	0.0	11.5 ^a	11.5
0.2727	0.9437	162.8	167.2
0.3861	0.9611	218.9	218.9
0.5132	0.9722	270.1	268.6
0.7933	0.9879	353.5	365.1
0.8879	0.9929	397.8	399.3
1.0	1.0	446.5	446.0

^a Literature data (12).

binary interaction parameters and correction factors for the modified Peng-Robinson equation of state will be useful in predicting the phase behavior of the above model systems. The accuracy is sufficient for most engineering calculations and indicates that the systems can be modeled using conventional equations of state.

Glossary

A, B, C	vapor pressure parameters in eq 1
AAPE	average absolute percent error
a	energy parameter in eq 4, atm cm ⁶ /mol ²
b	size parameter in eq 5, cm ³ /mol
C_a, C_b	correction factor
N	number of data
P	pressure, kPa
R	gas constant
T	temperature, K
V	molar volume, cm ³ /mol
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

α	adjustable binary parameter in eq 7
β	adjustable binary parameter in eq 7, cm ³ /mol
δ	Peng-Robinson binary interaction parameter in eq 6

Subscripts

calcd	calculated data
exptl	experimental data
i	component i
j	component j

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