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Vapor–Liquid Equilibria in the Systems of *n*-Decane/Tetralin, *n*-Hexadecane/Tetralin, *n*-Decane/1-Methylnaphthalene, and 1-Methylnaphthalene/Tetralin

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Vapor–liquid equilibrium data for the binary systems of *n*-decane/tetralin, *n*-hexadecane/tetralin, *n*-decane/1-methylnaphthalene, and 1-methylnaphthalene/tetralin were measured at a low to moderate pressure (0–1123 kPa) by using a static equilibrium cell. The binary *P*–*x* data were isothermally correlated using the modified Peng–Robinson equation of state to describe both vapor and liquid phases at 473.15, 533.15, and 573.15 K. Interaction parameters for density-dependent mixing rules are reported at each isotherm.

Introduction

The need for vapor–liquid equilibrium (VLE) data for mixtures of coal-derived liquids has been discussed previously (*1*–*14*). Such data would be invaluable in the design of process equipment involving the reaction or separation of coal liquids.

This present study is a continuation of efforts to develop a data base for aromatic and aromatic/aliphatic mixtures which may be present in coal liquefaction processes (*1*–*13*). High-temperature vapor–liquid equilibrium data for model mixtures representing coal-derived liquids are relatively scarce. In this paper the use of the modified Peng–Robinson equation of state (*15*, *16*) for correlating the data is presented.

Experimental Section

The experimental apparatus has been described previously (*18*, *19*). A 70-mL static equilibrium cell was used. A 50-mL sample of pure or binary liquid was charged to the evacuated stainless steel vessel such that the vapor space was quite small (5–20 mL). The pressure *P* exerted by this mixture was then measured as a function of temperature *T*. At the pressures reported in this study, the amount of material in the vapor phase was negligible, as verified by varying the amount of liquid charged to the cell. The accuracy of the data was limited by the purity of the liquids. The reported pressures are within 2% of the true values at the reported temperatures and compositions.

Table I. Comparison of Direct Experimental Vapor Pressures P_{expt} of Pure *n*-Decane, 1-Methylnaphthalene, Tetralin, and *n*-Hexadecane with Values P_{calc} Calculated Using the Coefficients *A*, *B*, and *C*, for Equation 1, as a Function of Temperature *T*, and Percentage Mean Relative Deviation, PMRD, Equation 2

		P_{calc}/kPa	
T/K	P_{expt}/kPa	this work	lit. (*19*, *20*)
	n-Decane		
409.0	34.0	34.0	34.3
449.0	103	103	106
488.1	254	253	259
526.8	533	532	539
566.4	1016	1016	1023
584.3	1320	1320	1332
this work: $A = 14.86$; $B = 4172.08$; $C = -40.99$; PMRD = 0.19			
refs 19 and 20: PMRD = 1.38			
	1-Methylnaphthalene		
485.0	45.2	45.2	47.2
523.6	113	113	116
559.5	228	231	234
580.6	336	335	337
594.8	423	424	425
this work: $A = 14.36$; $B = 4306.56$; $C = -76.87$; PMRD = 0.33			
refs 19 and 20: PMRD = 2.02			
	Tetralin		
464.8	71.7	71.7	74.3
498.6	155	155	159
516.0	221	221	224
532.3	300	300	303
562.4	503	503	503
579.7	659	659	655
this work: $A = 14.39$; $B = 4138.32$; $C = -56.01$; PMRD = 0.10			
refs 19 and 20: PMRD = 1.60			
	n-Hexadecane		
504.5	25.6	25.6	25.6
532.8	55.0	54.7	54.0
546.8	76.9	76.9	75.4
566.1	119	119	115
589.0	188	191	182
this work: $A = 15.00$; $B = 4817.50$; $C = -94.61$; PMRD = 0.46			
refs 19 and 20: PMRD = 2.06			

The following chemicals were used: *n*-hexadecane (29,631-7; 99+%), *n*-decane (D90-1; 99+%), tetralin (10,241-5; 99%), and 1-methylnaphthalene (M5680-8; 99%). All were supplied by Aldrich. As a secondary measure, the

Table II. Experimental Bubble Pressure P_{expt} of the *n*-Decane (1)/Tetralin (2) System at Mole Fraction x_1 of *n*-Decane as a Function of Temperature T, Coefficients A, B, and C, Equation 1, and Percentage Mean Relative Deviations, PMRD, Equation 2

T/K	P_{expt}/kPa	T/K	P_{expt}/kPa
x_1 = 0.206 04		x_1 = 0.404 92	
444.4	54.5	408.2	26.9
482.6	135	445.3	67.5
523.3	304	483.5	163
555.6	531	518.1	322
568.8	658	552.2	582
584.5	836	565.0	715
		585.0	970
A = 15.80		A = 15.958	
B = 5503.00		B = 5612.66	
C = 22.17		C = 32.96	
PMRD = 0.34		PMRD = 0.96	
x_1 = 0.603 77		x_1 = 0.803 88	
446.6	82.9	410.0	35.7
485.2	197	443.9	87.3
517.8	372	478.7	193
555.6	709	514.9	395
564.7	818	549.8	721
577.7	997	575.0	1073
		583.5	1213
A = 16.00		A = 16.18	
B = 5558.71		B = 5630.53	
C = 33.43		C = 36.90	
PMRD = 0.01		PMRD = 0.26	

Table III. Experimental Bubble Pressure P_{expt} of *n*-Hexadecane (1)/Tetralin (2) System at Mole Fraction x_1 of *n*-Hexadecane as a Function of Temperature T, Coefficients A, B, and C, Equation 1, and Percentage Mean Relative Deviations, PMRD, Equation 2

T/K	P_{expt}/kPa	T/K	P_{expt}/kPa
x_1 = 0.098 27		x_1 = 0.282 82	
483.3	99.0	405.0	10.2
524.4	232	438.7	25.9
562.0	453	478.5	74.5
581.1	609	514.2	158
599.2	797	553.4	327
		584.7	535
A = 15.10		A = 15.24	
B = 4916.15		B = 5236.07	
C = −15.25		C = 0.40	
PMRD = 0.28		PMRD = 1.33	
x_1 = 0.302 06		x_1 = 0.404 50	
413.6	12.1	452.4	26.2
442.8	28.5	492.4	70.0
495.6	103	530.2	152
536.0	229	568.6	300
570.8	411	581.2	365
606.6	707	599.2	487
A = 14.99		A = 15.24	
B = 5004.21		B = 5448.81	
C = −12.85		C = 2.54	
PMRD = 0.55		PMRD = 0.58	
x_1 = 0.5000		x_1 = 0.717 22	
448.2	19.3	485.8	22.6
488.2	47.1	516.0	47.3
533.0	113	553.4	98.8
570.8	213	567.5	131
601.6	337	588.2	191
A = 14.45		A = 14.80	
B = 5280.59		B = 5411.14	
C = 10.21		C = −22.37	
PMRD = 0.78		PMRD = 1.08	

components were analyzed by using gas chromatography (Hewlett-Packard 5880A) which showed the dominant peak to have an area of no less than 99% of the total. All chemicals were used without further purification.

Table IV. Experimental Bubble Pressure P_{expt} of the *n*-Decane (1)/1-Methylnaphthalene (2) System at Mole Fraction x_1 of *n*-Decane as a Function of Temperature T, Coefficients A, B, and C, Equation 1, and Percentage Mean Relative Deviations, PMRD, Equation 2

T/K	P_{expt}/kPa	T/K	P_{expt}/kPa
x_1 = 0.193 47		x_1 = 0.399 65	
452.6	34.1	440.7	45.0
489.2	79.2	484.8	123
529.7	175	520.3	243
559.3	298	555.6	447
572.4	371	574.4	591
581.7	432	592.4	762
A = 15.08		A = 15.23	
B = 5282.38		B = 5247.92	
C = 4.12		C = 18.69	
PMRD = 0.82		PMRD = 0.37	
x_1 = 0.603 29		x_1 = 0.803 36	
408.2	24.1	446.8	90.5
448.8	71.6	483.3	201
487.8	171	521.1	418
526.3	360	558.3	773
559.3	629	575.6	1010
574.4	792	593.3	1302
592.4	1035		
A = 15.66		A = 15.77	
B = 5328.46		B = 5322.93	
C = 18.84		C = 25.56	
PMRD = 0.23		PMRD = 0.28	

Table V. Experimental Bubble Pressure P_{expt} of the 1-Methylnaphthalene (1)/Tetralin (2) System at Mole Fraction x_1 of 1-Methylnaphthalene as a Function of Temperature T, Coefficients A, B, and C, Equation 1, and Percentage Mean Relative Deviations, PMRD, Equation 2

T/K	P_{expt}/kPa	T/K	P_{expt}/kPa
x_1 = 0.199 88		x_1 = 0.399 42	
444.4	36.8	442.7	28.0
484.7	97.8	480.5	71.3
509.4	163	515.2	160
548.8	345	549.5	304
571.4	504	574.4	468
592.1	696	592.4	620
A = 15.61		A = 15.80	
B = 5466.95		B = 5629.57	
C = 10.96		C = 9.01	
PMRD = 0.20		PMRD = 0.92	
x_1 = 0.603 16		x_1 = 0.803 32	
446.4	26.9	413.4	7.4
478.2	59.4	443.3	18.5
517.9	143	460.4	29.6
549.8	268	482.6	54.5
571.4	388	512.8	108
585.1	483	555.6	253
		568.2	316
		588.2	446
A = 15.68		A = 15.91	
B = 5645.32		B = 5816.80	
C = 9.52		C = 4.91	
PMRD = 0.65		PMRD = 0.84	

Results and Discussion

The vapor pressure and the bubble pressure measurements of all the systems are shown in Tables I–V. Pure components P–T data were fitted with a three-constant Antoine equation (1)

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

$$\mathrm{PMRD} = \left(\sum_{i}^{N} \frac{|P_{expt} - P_{calc}|}{P_{expt}} \right) \frac{100}{N} \tag{2}$$

with a percentage mean relative deviation (PMRD), eq 2, of less

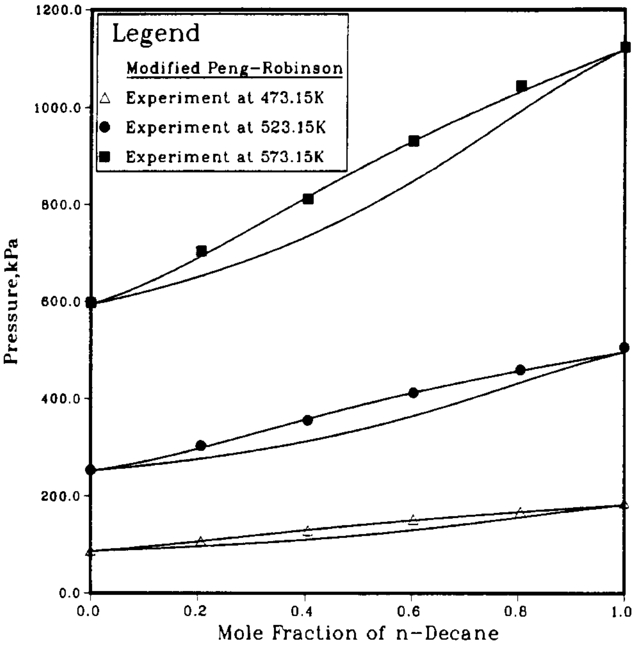

Figure 1. Equilibrium pressure vs composition diagram for the *n*-decane/tetralin system.

than 1.6% between correlated and experimental pressures. Comparison with literature values (*19*, *20*) indicates that the experimental errors in pure systems ranged from 1 to 3% (pressure), depending on the system.

In this work, the P-x-T data were regressed to determine the binary interaction parameters for the Peng-Robinson equation of state (P-R EOS) by using the density-dependent mixing rules (*15*, *16*). The following mixing rules were used for the modified P-R EOS.

$$b = \sum_i x_i b_i \tag{3}$$

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{4}$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - \delta_{ij}) \tag{5}$$

$$\delta_{ij} = \alpha_{ij} + \beta_{ij}/V \tag{6}$$

Equation 6 requires that the interaction parameter δ_{ij} vary linearly with the phase molar volume of the mixture. 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. Details of the modified P-R EOS are given in the preceding paper of this series (*18*).

The interaction parameters were taken as those values which minimized the following objective function

$$Q = \sum_i^N \frac{|P_{\text{expt}} - P_{\text{calc}}|}{P_{\text{expt}}} \tag{7}$$

Figures 1-3 show the isothermal P-x-y data correlated with the modified P-R EOS. The data can be accurately correlated with the modified P-R EOS for the *n*-decane/tetralin, *n*-decane/1-methylnaphthalene, and 1-methylnaphthalene/tetralin system, as shown in Figures 1-3. Differences between experimental and calculated pressures are generally less than 2%, except for the *n*-hexadecane/tetralin system which may form an azeotrope at 573.15 K. The Peng-Robinson parameters and correction factors at several temperatures are given in Tables VI and VII, and isothermal data at one temperature per system are given in Table VIII. Note that the results are insensitive to the values used for C_a and C_b. These parameters could be set to 1.0, but the values reported allow the pure

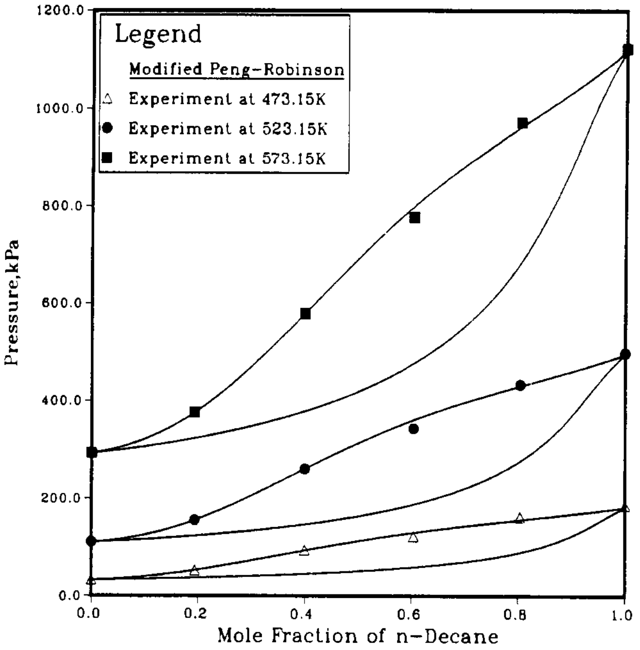

Figure 2. Equilibrium pressure vs composition diagram for the *n*-decane/1-methylnaphthalene system.

Table VI. 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
	1-Methylnaphthalene	
473.15	0.9861	0.9658
523.15	0.9788	0.9707
573.15	0.9506	0.9713
	Tetralin	
473.15	0.8947	0.9606
523.15	0.8529	0.9584
573.15	0.7496	0.9493
	n-Decane	
473.15	0.9094	0.9647
523.15	0.8250	0.9557
573.15	0.3968	0.9301
	n-Hexadecane	
473.15	0.7643	0.8935
523.15	0.7486	0.9062
573.15	0.6867	0.9115

Table VII. Interaction Parameters[a] for the Peng-Robinson Equation of State

T/K	α_{12}	β_{12}/(cm^3/mol)	PMRD
	1-Methylnaphthalene (1)/Tetralin (2)		
473.15	0.370 951	-135.225	1.29
523.15	0.367 875	-139.389	1.05
573.15	0.322 000	-126.932	0.64
	n-Decane (1)/Tetralin (2)		
473.15	0.065 4156	-38.6131	0.98
523.15	0.089 8000	-53.2062	0.88
573.15	0.089 9023	-54.7473	0.72
	n-Decane (1)/1-Methylnaphthalene (2)		
473.15	0.159 609	-97.5048	2.48
523.15	0.220 852	-132.306	1.14
573.15	0.220 784	-141.059	0.73
	n-Hexadecane (1)/Tetralin (2)		
473.15	-0.312 969	92.5902	2.69
523.15	-0.440 258	155.091	2.66
573.15	-0.238 072	58.2270	8.7

[a] $\delta_{12} = \alpha_{12} + \beta_{12}/V$.

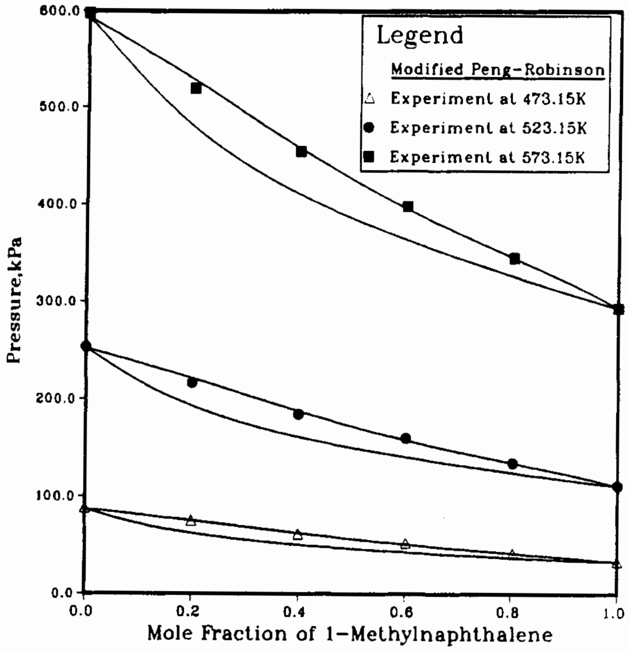

Figure 3. Equilibrium pressure vs composition diagram for the 1-methylnaphthalene/tetralin system.

Table VIII. Isothermal Vapor–Liquid Equilibrium Data

$x_{1\,\mathrm{expt}}$	$y_{1\,\mathrm{calc}}$	P_{expt}/kPa	P_{calc}/kPa
1-Methylnaphthalene (1)/Tetralin (2) at T = 523.15 K			
0.0	0.0	254	252
0.199 88	0.090 10	217	221
0.399 42	0.225 66	185	188
0.601 36	0.427 14	160	158
0.803 32	0.674 59	134	134
1.0	1.0	112	111
n-Decane (1)/Tetralin (2) at T = 523.15 K			
0.0	0.0	254	252
0.206 04	0.335 41	304	299
0.404 92	0.583 21	356	359
0.603 77	0.745 68	412	412
0.803 88	0.872 68	459	458
1.0	1.0	506	496
n-Decane (1)/1-Methylnaphthalene (2) at T = 523.15 K			
0.0	0.0	112	111
0.193 47	0.455 21	156	156
0.399 65	0.778 37	261	261
0.603 29	0.892 58	344	361
0.803 36	0.944 40	434	431
1.0	1.0	499	496
n-Hexadecane (1)/Tetralin (2) at T = 523.15 K			
0.0	0.0	254	252
0.098 27	0.007 39	227	238
0.282 82	0.028 85	189	181
0.302 06	0.033 39	181	173
0.404 50	0.071 75	132	132
0.500 00	0.140 89	93.5	99.0
0.717 22	0.490 12	54.6	54.6
1.0	1.0	43.1	42.5

component vapor pressures to be exactly reproduced. The isothermal data are obtained using eq 1 to correct for slight deviations in temperature from the specified value.

Glossary

A,B,C	vapor pressure parameters, eq 1
a	energy parameter in Peng–Robinson equation of state, atm cm^6/mol^2
b	size parameter in Peng–Robinson equation of state, cm^3/mol
C_a	correction factor in the Peng–Robinson equation of state
C_b	correction factor in the Peng–Robinson equation of state
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
β	adjustable binary parameter, cm^3/mol
δ	Peng–Robinson binary interaction parameter

Subscripts

calc	calculated value
expt	experimental value
i	component i
j	component j

Registry No. n-Decane, 124-18-5; tetralin, 119-64-2; n-hexadecane, 544-76-3; 1-methylnaphthalene, 90-12-0.

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