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Isothermal Vapor–Liquid Equilibrium of Binary and Ternary Systems Composed of Heavy Aromatic Compounds

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Isothermal vapor–liquid equilibrium (VLE) data for four binary and eight ternary systems composed of polynuclear aromatic compounds have been measured at 170 and 190 °C using a dynamic equilibrium still. Binary VLE data are correlated by two different liquid-phase activity coefficient models, i.e., UNIQUAC and Margules using the maximum likelihood method to determine the binary interaction parameters. The binary interaction parameters obtained from this and our previous studies are used to predict the VLE for ternary mixtures using the same two models. Either of the models can predict the bubble point pressure within 10 mmHg and vapor-phase mole fractions within 0.03 mole fraction. The measured VLE data for the ternary systems are also compared with those predicted using Scatchard–Hildebrand regular solution theory. The regular solution theory predicts the bubble point pressures within an average absolute difference of 6 mmHg and vapor-phase mole fractions within 0.03 mole fraction.

Introduction

Liquid hydrocarbons derived from coal provide an alternative to petroleum as a source of feedstocks for refineries and petrochemical plants. These liquid mixtures contain high molecular weight aromatic compounds, and vapor–liquid equilibrium (VLE) data for such compounds are relatively scarce, especially at high temperatures (*1*). The purpose of this research is to determine vapor–liquid equilibrium data for ternary systems containing heavy aromatic compounds and to test the ability of various thermodynamic activity coefficient models derived from binary data to predict the ternary results. These data are useful in the design of coal liquefaction processes and also in the processing of heavy crude oil or tar sands.

This work reports isothermal VLE data for four binary and eight ternary systems at 170 and 190 °C. The compounds studied are *cis*-decalin, tetralin, 1-methylnaphthalene, naphthalene, biphenyl, acenaphthene, dibenzofuran, and phenanthrene. VLE for systems containing these compounds are difficult to study since some of the compounds are solid at room temperature (*2*). This work is a continuation of our studies on the vapor–liquid equilibrium of heavy aromatic compounds (*3*). We are not aware of any VLE data in the literature for the systems presented in this study.

Experimental Section

All the chemicals used in this study were purchased from Aldrich Chemical Co. The solid and liquid samples were further purified as described in ref 3. The final purities of the compounds as obtained by gas chromatography (GC) (area %) were as follows: 99.72%, *cis*-decalin; 99.69%, tetralin; 99.85%, 1-methylnaphthalene; 99.89%, naphthalene; 99.97%, biphenyl; 99.58%, acenaphthene; 99.78%, dibenzofuran; and 99.13%, phenanthrene.

Vapor–liquid equilibria for binary and ternary systems containing these compounds were measured using a recirculating still supplied by Fisher of FRG. The operation of this still has been described previously (*2–4*). Vapor and liquid were brought to equilibrium in the still at a measured temperature and pressure. Vapor and liquid samples were analyzed by gas chromatography using a flame ionization detector. The GC column was a 50% phenyl methyl silicone glass capillary column with 0.53-mm i.d., 2-μm coating, and 10-m length, supplied by Hewlett-Packard.

Table I. Vapor Pressure $P°$ Data of 1-Methylnaphthalene as a Function of Temperature t

t/°C	$P°$/mmHg	t/°C	$P°$/mmHg	t/°C	$P°$/mmHg
194.6	222	180.1	146	171.7	113
192.0	206	178.0	137	170.1	107
190.0	195	176.4	131	169.5	105
187.3	180	174.5	123	167.6	99
183.6	162	172.8	117	165.3	92

Antoine Constants, Equation 1
$A = 12.7585$ $B = -2015.13$ $C = 79.706$

The accuracies in our temperature and pressure measurements are ±0.1 °C and ±1.0 mmHg, respectively. The accuracy in composition analysis is ±0.0025 mole fraction (*3*).

Results and Discussion

Table I shows measured vapor pressure data for 1-methylnaphthalene. The vapor pressures of other compounds used in this study have already been measured and are reported in our previous study (*3*). These vapor pressure, $P_i°$, data were regressed using a three-constant Antoine equation of the type

$$\ln (P_i°/\text{mmHg}) = A + B/[(t/°\text{C}) + C] \qquad (1)$$

where t is the temperature. The three constants for 1-methylnaphthalene are also reported in Table I. In the range of temperature studied, experimental vapor pressure data agreed with the literature (*5*) values within 0.5%.

Analysis of Data for the Binary Mixtures**.** Table II presents the binary VLE data for four systems at 190 °C. Figure 1 shows data for the tetralin–1-methylnaphthalene system as an illustration.

The binary VLE data were first tested for thermodynamic consistency using the method of Fredenslund (*6*). A four-parameter Legendre polynomial was used for the excess Gibbs free energy. The measured binary data were considered to be consistent when the absolute difference between calculated and measured mole fractions of component 1 in the vapor phase was less than 0.01. The results of this test are shown in Table III. It is clear from this table that the data of this study are thermodynamically consistent.

The binary systems do not deviate greatly from ideal solution behavior. Raoult's law predicts pressure within 12 mmHg and vapor composition within 0.02 mole fraction. To seek a closer fit, the binary data were regressed using the maximum likelihood procedure of Prausnitz et al. (*7*) to determine the binary parameters A_{12} and A_{21}, for two different thermodynamic liquid-phase activity coefficient models, i.e., UNIQUAC (*8*) and Margules. The details of this regression procedure were presented in our previous paper (*3*). The UNIQUAC equation was used because it has a wide range of applicability. The Margules equation was used because it is a simple empirical model.

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Table II. Vapor–Liquid Equilibrium Data for Binary Systems: Pressure P, Temperature T, Liquid-Phase Mole Fraction x_1, and Vapor-Phase Mole Fraction y_1

P/mmHg	t/°C	x_1	y_1
Tetralin (1)–1-Methylnaphthalene (2)			
495	190.0	0.9862	0.9921
468	190.0	0.9029	0.9612
435	190.0	0.7847	0.9067
408	190.0	0.6916	0.8520
375	190.0	0.5849	0.7816
336	190.0	0.4539	0.6768
300	190.0	0.3402	0.5670
269	190.1	0.2371	0.4455
250	190.0	0.1739	0.3562
225	190.0	0.0900	0.2097
203	190.0	0.0261	0.0554
1-Methylnaphthalene (1)–Naphthalene (2)			
199	190.0	0.9851	0.9657
226	189.9	0.8811	0.7633
240	190.0	0.8224	0.6790
259	190.0	0.7486	0.5669
277	190.0	0.6599	0.4690
291	190.0	0.5878	0.4028
312	190.1	0.4723	0.3150
332	190.0	0.3610	0.2410
347	190.1	0.2684	0.1754
1-Methylnaphthalene (1)–Biphenyl (2)			
194	190.0	0.9670	0.9730
191	190.0	0.8814	0.9004
188	190.0	0.7968	0.8297
186	190.0	0.7182	0.7632
182	190.0	0.6282	0.6886
179	190.0	0.5416	0.6145
173	190.0	0.4227	0.5013
168	190.0	0.3321	0.4125
161	190.0	0.2268	0.2956
156	190.0	0.1714	0.2222
1-Methylnaphthalene (1)–Acenaphthene (3)			
193	190.0	0.9795	0.9857
184	190.0	0.9058	0.9539
177	190.0	0.8334	0.9183
168	190.0	0.7480	0.8779
157	190.0	0.6403	0.8101
148	190.0	0.5518	0.7490
138	190.0	0.4601	0.6789
125	190.0	0.3410	0.5655
110	190.0	0.2261	0.4093
101	190.0	0.1677	0.3001

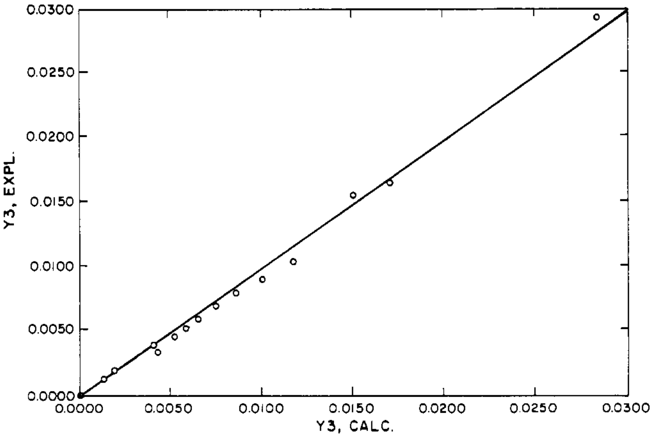

Figure 1.

To determine binary parameters using the maximum likelihood method, vapor-phase nonidealities were obtained by using second virial coefficients as given by Hayden and O'Connell (*9*). Liquid molar volumes were calculated using the modified Rackett equation, as described in ref 7. Critical constants were taken from the literature whenever available; otherwise they were calculated from empirical correlations (*10*). These thermodynamic properties are reported in our previous paper (*3*) for all the compounds used in this study except for 1-methylnaphthalene. The properties for 1-methylnaphthalene used in the VLE data analysis were critical temperature t_c = 498.15 °C (*12*), critical pressure P_c = 36.0 bar (*12*), critical volume V_c = 462.0 cm^3 mol^{-1} (*12*), Rackett parameter ZRA = 0.2634 (*14*), radius of gyration R_d = 4.346 Å, dipole moment D_p = 0.5 D (*12*), UNIQUAC area structure parameter q = 4.001 (*15*), and UNIQUAC volume structure parameter r = 5.716 (*15*).

Table III. Results of Thermodynamic Consistency Test for Systems Involving 1-Methylnaphthalene at 190 °C

system	RMSD(P)^a/ mmHg	RMSD(y_1)^a
tetralin (1)–1-methylnaphthalene (2)	0.66	0.0062
1-methylnaphthalene (1)–naphthalene (2)	0.50	0.0070
1-methylnaphthalene (1)–biphenyl (2)	0.26	0.0068
1-methylnaphthalene (1)–acenaphthene (2)	0.28	0.0098

[a] Root mean square deviations: $\mathrm{RMSD}(P) = [(1/N)\sum_{i=1}^{N}(P_{\mathrm{calc}} - P_{\mathrm{expt}})^2]^{1/2}$; $\mathrm{RMSD}(y_1) = [(1/N)\sum_{i=1}^{N}(y_{1,\mathrm{calc}} - y_{1,\mathrm{expt}})^2]^{1/2}$.

Table IV reports the binary parameters and the mean deviations between calculated and experimental temperature, pressure, and liquid- and vapor-phase mole fractions for the four systems studied at 190 °C using the maximum likelihood method and the two different models. Each model gives a good fit of the binary data. Absolute average difference (AAD) values obtained for pressure, temperature, and liquid-phase mole fractions are generally within the experimental error, although for one system, i.e., 1-methylnaphthalene–acenaphthene, the AAD in the pressure is greater than expected (1.5 mmHg). The AAD in vapor-phase mole fractions for all four systems were found to be larger than the accuracy of the gas chromatographic analysis. We suspect the error associated with the vapor samples to be higher than for liquid samples because of condensation of the heavy component in the condenser.

Ternary Data. Table V reports ternary VLE data for five compounds, i.e., naphthalene, biphenyl, acenaphthene, dibenzofuran, and phenanthrene with *cis*-decalin and tetralin at 170 °C. Table VI reports ternary VLE data for three compounds, i.e., naphthalene, biphenyl, and acenaphthene with tetralin and 1-methylnaphthalene at 190 °C.

Many researchers in the past 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 systems containing coal liquid compounds, we used the binary interaction parameters obtained from this study and our previous work (*3*) to predict the bubble point pressure and vapor-phase mole fractions of components of our ternary systems. The equations used to determine the activity coefficients for any component of the ternary mixtures using the UNIQUAC and Margules models were taken from ref 11.

Table VII lists the average absolute deviations (AADs) between experimental and calculated pressures and vapor-phase mole fractions of components of the ternary mixtures for all eight systems using the UNIQUAC and Margules models for the excess Gibbs free energy. The predictions of bubble point pressure and vapor-phase mole fraction generally agree with experiment within 10 mmHg and 0.03 mole fraction, respectively.

Figure 2 is a comparison of experimental vapor-phase mole fractions of naphthalene with those calculated using parameters from binary data and the UNIQUAC model for the system

Table IV. Binary Parameters and Absolute Average Deviations (AAD) from Regression of Binary VLE Data at 190 °C

			AAD			
model	A_{12}[a]	A_{21}[a]	P/mmHg	t/°C	x_1	y_1
		Tetralin (1)–1-Methylnaphthalene (2)				
UNIQUAC	976.17	−835.16	0.45	0.01	0.0005	0.0037
Margules	0.02858	0.04665	0.46	0.01	0.0005	0.0037
		1-Methylnaphthalene (1)–Naphthalene (2)				
UNIQUAC	48.88	201.01	0.58	0.02	0.0007	0.0044
Margules	0.25005	0.19759	0.62	0.02	0.0007	0.0048
		1-Methylnaphthalene (1)–Biphenyl (2)				
UNIQUAC	643.84	−470.80	0.53	0.01	0.0003	0.0021
Margules	0.12582	0.15292	0.59	0.01	0.0003	0.0021
		1-Methylnaphthalene (1)–Acenaphthene (2)				
UNIQUAC	3128.06	−2199.88	1.44	0.02	0.0006	0.0042
Margules	−0.07796	0.14641	1.38	0.02	0.0006	0.0051

[a] Parameter listed is dimensionless for the Margules model and in joules per mole for the UNIQUAC model.

Table V. Ternary Vapor–Liquid Equilibrium Data: Pressure P, Temperature t, Liquid-Phase Mole Fraction x_i, and Vapor-Phase Mole Fraction y_i with *cis*-Decalin (1) and Tetralin (2)

P/mmHg	t/°C	x_2	y_2	x_3	y_3	P/mmHg	t/°C	x_2	y_2	x_3	y_3
					Naphthalene (3)						
397	170.0	0.0375	0.0333	0.0203	0.0183	319	170.0	0.6480	0.5747	0.1230	0.0909
393	170.0	0.0966	0.0767	0.0093	0.0063	316	170.0	0.2844	0.2642	0.4233	0.3065
390	170.0	0.0896	0.0704	0.0543	0.0383	306	170.0	0.8142	0.7812	0.0714	0.0525
374	170.0	0.1706	0.1340	0.1231	0.0851	301	169.9	0.4007	0.3914	0.4068	0.3021
362	170.0	0.2067	0.1675	0.1938	0.1337	287	170.0	0.8972	0.9155	0.0982	0.0764
352	170.0	0.3027	0.2517	0.1925	0.1349	287	169.9	0.3167	0.3327	0.5336	0.4069
339	169.9	0.3882	0.3380	0.2167	0.1531	277	169.8	0.2310	0.2506	0.6410	0.5118
335	169.9	0.4531	0.3979	0.1783	0.1263	271	170.0	0.2918	0.3235	0.6100	0.5007
325	170.0	0.3244	0.2913	0.3475	0.2415	244	170.0	0.1626	0.2154	0.8117	0.7232
321	170.0	0.7242	0.6624	0.0617	0.0490						
					Biphenyl (3)						
399	170.0	0.0436	0.0360	0.0064	0.0026	285	170.0	0.0782	0.0808	0.3899	0.1166
395	170.0	0.0196	0.0165	0.0255	0.0095	275	170.0	0.8235	0.8752	0.1241	0.0353
375	170.1	0.0543	0.0468	0.0850	0.0230	266	170.1	0.6508	0.7135	0.2258	0.0698
367	170.1	0.0726	0.0608	0.1086	0.0299	259	170.1	0.1685	0.1887	0.4402	0.1386
356	170.0	0.0821	0.0724	0.1472	0.0403	257	170.1	0.0887	0.1015	0.4807	0.1551
355	170.1	0.0702	0.0651	0.1125	0.0243	234	170.1	0.5025	0.6286	0.3789	0.1288
352	170.1	0.1457	0.1273	0.1408	0.0401	221	170.0	0.0676	0.0886	0.6037	0.2190
323	170.1	0.1023	0.0974	0.2561	0.0680	176	170.1	0.4004	0.6678	0.5714	0.2499
298	170.1	0.9435	0.9214	0.0128	0.0104	149	170.0	0.0422	0.0834	0.8154	0.4231
290	170.1	0.2114	0.2169	0.3273	0.0956						
					Acenaphthene (3)						
396	170.0	0.0215	0.0183	0.0141	0.0018	291	170.1	0.7657	0.7703	0.0989	0.0153
373	170.0	0.0849	0.0761	0.0674	0.0079	272	170.0	0.8956	0.9603	0.0900	0.0145
354	170.0	0.1774	0.1493	0.0931	0.0100	250	170.1	0.3242	0.3806	0.3733	0.0676
326	170.0	0.2012	0.1726	0.1761	0.0295	235	170.0	0.2964	0.3697	0.4250	0.0811
314	170.0	0.3147	0.2761	0.1956	0.0302	224	170.0	0.3866	0.5039	0.4180	0.0823
304	170.0	0.7045	0.6801	0.0881	0.0133	194	170.0	0.3643	0.5500	0.5032	0.1128
301	170.0	0.4634	0.4556	0.1823	0.0283	166	170.0	0.2544	0.4505	0.6182	0.1610
301	170.0	0.6345	0.6182	0.1201	0.0182	145	170.0	0.2875	0.5840	0.6501	0.1915
295	170.0	0.3552	0.3342	0.2060	0.0383	110	170.0	0.1853	0.5022	0.7748	0.3008
					Dibenzofuran (3)						
399	170.0	0.0226	0.0160	0.0108	0.0044	287	170.0	0.6419	0.6587	0.1799	0.0363
385	170.0	0.0460	0.0385	0.0458	0.0121	279	170.0	0.4243	0.4398	0.2963	0.0643
362	170.0	0.0631	0.0545	0.1264	0.0286	272	170.0	0.0999	0.1083	0.4582	0.1008
344	170.0	0.0871	0.0734	0.1844	0.0403	266	170.2	0.8353	0.9402	0.1360	0.0312
343	170.0	0.2305	0.2012	0.1458	0.0307	259	170.0	0.3685	0.4853	0.3778	0.0870
341	170.0	0.3500	0.3042	0.1166	0.0254	217	170.1	0.3207	0.4770	0.5175	0.1318
331	170.3	0.5206	0.4503	0.1088	0.0228	202	170.1	0.2087	0.3491	0.6264	0.1654
292	170.0	0.4243	0.4209	0.2568	0.0578	172	170.0	0.2154	0.4429	0.6869	0.2064
287	170.0	0.5300	0.5463	0.2286	0.0303	116	170.1	0.1728	0.5601	0.8077	0.3403
					Phenanthrene (3)						
382	170.0	0.0414	0.0343	0.0445	0.0017	277	170.0	0.6521	0.6843	0.1947	0.0068
364	170.0	0.0549	0.0494	0.0970	0.0037	266	170.0	0.8133	0.9236	0.1366	0.0044
340	169.9	0.0641	0.0772	0.1604	0.0057	255	169.9	0.0782	0.1012	0.4281	0.0164
337	170.1	0.3233	0.2944	0.1093	0.0031	255	170.0	0.4292	0.5258	0.2989	0.0102
335	169.9	0.2068	0.1947	0.1463	0.0049	236	170.0	0.3692	0.5124	0.3734	0.0155
297	170.0	0.9039	0.9096	0.0366	0.0011	172	169.9	0.1796	0.3592	0.6001	0.0291
282	169.9	0.3519	0.3896	0.2607	0.0089	83	170.0	0.1190	0.7334	0.8529	0.0807
280	170.0	0.4608	0.4943	0.2236	0.0077						

Table VI. Ternary Vapor–Liquid Equilibrium Data: Pressure P, Temperature t, Liquid-Phase Mole Fraction x_i, and Vapor-Phase Mole Fraction y_i with Tetralin (1) and 1-Methylnaphthalene (2)

P/mmHg	t/°C	x_2	y_2	x_3	y_3
		Naphthalene (3)			
489	190.0	0.0287	0.0115	0.0148	0.0112
481	190.0	0.0471	0.0196	0.0492	0.0421
466	190.0	0.0892	0.0391	0.0940	0.0802
456	190.0	0.1100	0.0443	0.1677	0.1501
437	190.0	0.1697	0.0709	0.1757	0.1668
434	189.9	0.1116	0.0497	0.3791	0.3517
403	190.0	0.2962	0.1468	0.1320	0.1389
370	190.1	0.2385	0.1387	0.5957	0.6548
365	189.9	0.2272	0.1385	0.6487	0.7097
348	190.0	0.4456	0.2473	0.2362	0.3018
355	189.9	0.3564	0.1981	0.4749	0.5556
341	190.1	0.4214	0.2419	0.3737	0.4630
333	190.0	0.4700	0.2784	0.3147	0.3870
246	190.0	0.8140	0.6462	0.1222	0.2425
237	190.0	0.8542	0.7202	0.0304	0.0662
		Biphenyl (3)			
461	189.9	0.0484	0.0199	0.0703	0.0219
439	190.0	0.1104	0.0435	0.0904	0.0308
423	190.0	0.1248	0.0571	0.1161	0.0398
387	190.0	0.1785	0.1085	0.1699	0.0594
367	190.0	0.2958	0.1582	0.1251	0.0495
343	189.9	0.1199	0.0748	0.3549	0.1358
312	190.0	0.3047	0.2017	0.2836	0.1163
283	190.0	0.5005	0.3115	0.1695	0.1157
274	189.9	0.4308	0.3070	0.2607	0.1372
260	190.0	0.6362	0.4723	0.1479	0.0856
259	190.0	0.3889	0.3029	0.3482	0.1831
238	190.0	0.3136	0.2751	0.4602	0.2648
206	190.1	0.8256	0.7950	0.1247	0.0965
196	189.9	0.8346	0.8493	0.1511	0.1124
166	190.1	0.1342	0.1871	0.8120	0.6716
		Acenaphthene (3)			
486	190.0	0.0258	0.0092	0.0133	0.0023
464	190.0	0.0669	0.0275	0.0380	0.0065
430	190.0	0.1273	0.0529	0.0763	0.0140
408	190.1	0.1366	0.0639	0.1205	0.0236
380	190.0	0.1685	0.0940	0.1533	0.0339
364	190.0	0.2774	0.1438	0.1452	0.0279
299	190.0	0.3304	0.2187	0.2305	0.0627
272	190.0	0.4639	0.3256	0.2021	0.0626
252	190.0	0.6238	0.4741	0.1383	0.0455
233	189.9	0.4156	0.3555	0.3241	0.1103
228	189.9	0.2924	0.2649	0.4227	0.1434
211	189.9	0.3140	0.3072	0.4422	0.1661
199	189.9	0.8051	0.8020	0.1221	0.0547
171	189.9	0.2194	0.2600	0.5882	0.2638
166	190.0	0.2360	0.3106	0.5899	0.2892

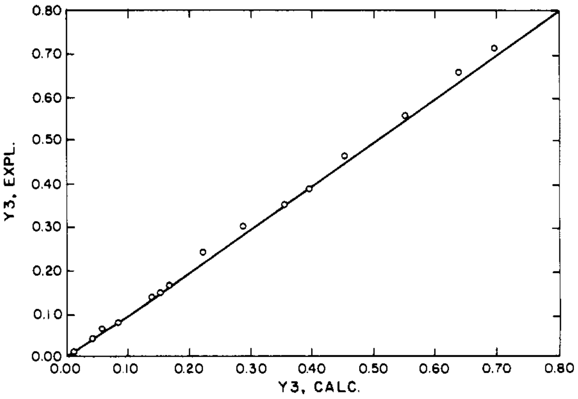

Figure 2.

tetralin (1)–1-methylnaphthalene (2)–naphthalene (3) at 190 °C. Figure 3 compares phenanthrene vapor-phase mole fractions using the Margules model for the system *cis*-decalin (1)–tetralin (2)–phenanthrene (3).

Table VII. Comparison of Ternary Data with Those Calculated Using Binary Data and Different Models

t/°C	model	AAD(P)^a/mmHg	AAD(y_1)$_a$	AAD(y_2)^a	AAD(y_3)^a
	cis-Decalin (1)–Tetralin (2)–Naphthalene (3)				
170.0	UNIQUAC	1.5	0.0076	0.0067	0.0095
	Margules	1.1	0.0081	0.0061	0.0099
	Regu. Sol.	3.5	0.0084	0.0064	0.0096
	Ideal Sol.	11.4	0.0181	0.0116	0.0113
	cis-Decalin (1)–Tetralin (2)–Biphenyl (3)				
170.0	UNIQUAC	1.5	0.0027	0.0020	0.0031
	Margules	1.8	0.0031	0.0029	0.0032
	Regu. Sol.	2.1	0.0031	0.0016	0.0032
	Ideal Sol.	10.0	0.0014	0.0094	0.0067
	cis-Decalin (1)–Tetralin (2)–Acenaphthene (3)				
170.0	UNIQUAC	2.6	0.0058	0.0050	0.0030
	Margules	3.0	0.0072	0.0050	0.0032
	Regu. Sol.	3.0	0.0091	0.0052	0.0032
	Ideal Sol.	9.7	0.0233	0.0216	0.0040
	cis-Decalin (1)–Tetralin (2)–Dibenzofuran (3)				
170.0	UNIQUAC	8.9	0.0151	0.0049	0.0067
	Margules	7.3	0.0165	0.0180	0.0059
	Regu. Sol.	4.6	0.0147	0.0156	0.0052
	Ideal Sol.	21.5	0.0270	0.0234	0.0136
	cis-Decalin (1)–Tetralin (2)–Phenanthrene (3)				
170.0	UNIQUAC	4.5	0.0028	0.0299	0.0021
	Margules	4.5	0.0270	0.0289	0.0022
	Regu. Sol.	4.0	0.0263	0.0283	0.0021
	Ideal Sol.	16.0	0.0125	0.0150	0.0042
	Tetralin (1)–1-Methylnaphthalene (2)–Naphthalene (3)				
190.0	UNIQUAC	2.3	0.0099	0.0071	0.0076
	Margules	2.4	0.0098	0.0074	0.0077
	Regu. Sol.	5.5	0.0101	0.0069	0.0106
	Ideal Sol.	8.6	0.0106	0.0071	0.0124
	Tetralin (1)–1-Methylnaphthalene (2)–Biphenyl (3)				
190.0	UNIQUAC	3.4	0.0114	0.0101	0.0099
	Margules	3.3	0.0112	0.0101	0.0101
	Regu. Sol.	4.1	0.0092	0.0107	0.0096
	Ideal Sol.	3.8	0.0075	0.0106	0.0081
	Tetralin (1)–1-Methylnaphthalene (2)–Acenaphthene (3)				
190.0	UNIQUAC	10.2	0.0133	0.0208	0.0114
	Margules	6.0	0.0178	0.0151	0.0034
	Regu. Sol.	5.2	0.0167	0.0154	0.0039
	Ideal Sol.	4.9	0.0174	0.0150	0.0035

[a] AAD = average absolute deviation: $\mathrm{AAD}(P) = (1/N)(\sum_{i=1}^{N}|(P_{\mathrm{calc}} - P_{\mathrm{expt}})|)$; $\mathrm{AAD}(y_i) = (1/N)(\sum_{i=1}^{N}|(y_{i,\mathrm{calc}} - y_{i,\mathrm{expt}})|)$.

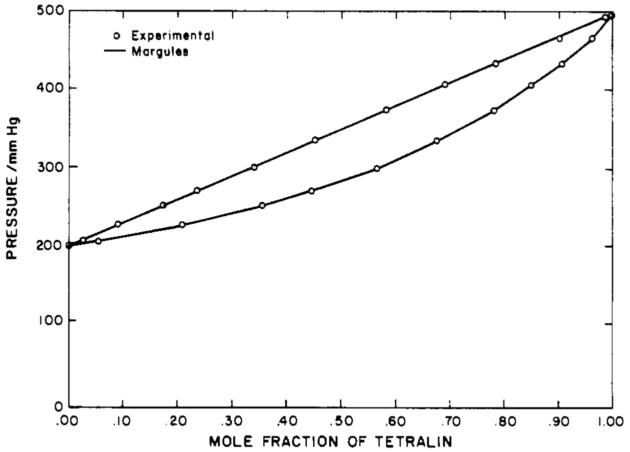

Figure 3.

For practical applications, the regular solution theory equations provide a simple way of predicting VLE data for mixtures of nonpolar compounds. Therefore, we used these equations (*11*) to predict bubble point pressures and vapor-phase mole

Table VIII. Solubility Parameters ($(J/cm^3)^{1/2}$) and Liquid Molar Volumes (cm^3/mol) of the Compounds at the Melting Point of the Solids

		solids		*cis*-decalin		tetralin		1-methyl-naphthalene	
	t_m/°C	δ_2	v_2^l	δ_1	v_1^l	δ_1	v_1^l	δ_1	v_1^l
naphthalene	79.65	19.67[a]	130.9[g]	16.36[a]	165.6[e]	18.15[a]	143.0[d]	18.51[b]	153.1[e]
biphenyl	69.45	19.30[a]	155.2[d]	16.59[a]	163.9[e]	18.37[a]	141.9[d]	18.70[b]	151.9[e]
acenaphthene	93.15	18.93[c]	149.8[h]	16.24[a]	167.7[e]	17.87[a]	144.7[d]	18.30[b]	154.7[e]
dibenzofuran	82.55	20.41[f]	152.5[i]	16.37[a]	166.2[e]	18.10[a]	143.4[d]		
phenanthrene	99.65	19.77[a]	168.1[j]	16.00[a]	169.5[e]	17.74[a]	145.4[d]		

[a] Enthalpy of vaporization was calculated using the Clausius–Clapeyron equation with Antoine constants given by Reid et al. (*13*). [b] Enthalpy of vaporization was calculated using the Clausius–Clapeyron equation with Antoine constants given in Table I and our previous work (*3*). [c] Antoine constant given by Dean (*16*). [d] Timmermans (*17*). [e] Calculated using the modified Rackett (*7*) equation. [f] Carruth and Kobayashi (*18*). [g] Weast (*19*), Reid et al. (*13*), and Dean (*16*). [h] Lange and Forker (*20*). [i] Tsonopoulos et al. (*21*). [j] International Critical Tables (*22*). Extrapolated by using equation 12-3.2 of Reid et al. (*13*).

fractions for our ternary mixtures. Table VIII lists the values of solubility parameters and liquid molar volumes for the compounds used in this study. In accordance with a suggestion by Coon et al. (*2*), these parameters were evaluated at the melting points of the compounds in the first column. These components are solids at ambient temperature. Table VII reports the average absolute deviations between experimental and calculated pressures and vapor-phase mole fractions using regular solution theory. The regular solution theory predicted the bubble point pressures within 6 mmHg and vapor-phase mole fractions of the components of the ternary mixtures within 0.03 mole fraction for all the systems. This theory is attractive because of its simplicity. It does not require any experimental data on mixture vapor–liquid equilibria.

Table VII also shows the results of predictions by Raoult's law. Two of the systems, tetralin (1)–1-methylnaphthalene (2)–biphenyl (3) and tetralin (1)–1-methylnaphthalene (2)–acenaphthene (3), were adequately described by Raoult's law. For the other systems, agreement with experiment was improved significantly by using the various activity coefficient models.

Conclusion

Vapor–liquid equilibria for four binary systems have been measured and found to be thermodynamically consistent. These data are used to determine binary interaction parameters using the UNIQUAC and Margules models. Both models represent the data quite well.

The binary parameters obtained in this study and in our previous work are used to predict ternary vapor–liquid equilibrium curves using the same models and also regular solution theory. For these slightly nonideal systems, all of these models can be used to predict the ternary vapor–liquid equilibrium diagram.

Glossary

A	Antoine parameter in eq 1
A_{ij}	optimized parameters in UNIQUAC and Margules models
B	Antoine parameter in eq 1
C	Antoine parameter in eq 1
N	total number of data points
P	pressure, mmHg
P°	vapor pressure, mmHg
t	temperature, °C
t_m	melting point temperature, °C
v^l	molar volume of liquid, $cm^3\ mol^{-1}$
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Greek Letters

δ	solubility parameter
ω	acentric factor

Subscripts

i	component *i*
i,calc	calculated value of component *i*
i,expt	experimental value of component *i*
ij	mixture of components *i* and *j*

Registry No. Tetralin, 119-64-2; 1-methylnaphthalene, 90-12-0; naphthalene, 91-20-3; biphenyl, 92-52-4; acenaphthalene, 208-96-8; *cis*-decalin, 493-01-6; dibenzofuran, 132-64-9; phenanthrene, 85-01-8.

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