model can correlate this apparent negative deviation from Raoult's law (and the corresponding local maximum in the activity coefficient of the furan, required by the constraints of the Gibbs–Duhem equation). In contrast, the Van Laar model cannot reproduce maxima or minima of the activity coefficient as a function of composition. Such extrema have been documented, but they are unusual (one example is the chloroform/ethanol system). Considering the nature of the intermolecular forces in the 2-methylfuran/benzene system, extrema in the activity coefficients are much less likely than experimental errors on the order of one-tenth of 1%. We call attention to this detail because, while it is obvious to the engineer familiar with molecular thermodynamics, it may not be apparent to the process engineer whose day-to-day work is remote from fluid-phase equilibrium thermodynamics.

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Registry No. 2-Methylfuran, 534-22-5; cyclohexane, 110-82-7; benzene, 71-43-2; thiophene, 110-02-1; pyridine, 110-86-1.

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Supplementary Material Available: Analytical calibrations, standard deviations in measured quantities, and excess-Gibbs-energy-model parameters for the binary systems of 2-methylfuran with cyclohexane, benzene, thiophene, and pyridines (6 pages). Ordering information is given on any current masthead page.

Vapor–Liquid Equilibria for Model Mixtures of Coal-Derived Liquids. 2. Binary Systems with Bicyclic and High-Boiling Fluids

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Vapor–liquid equilibria were measured for binary systems in the temperature range 150–237 °C. Five systems were studied: quinoline/1-methylnaphthalene, quinoline/*m*-cresol, tetralin/*m*-cresol, benzothiazole/*m*-cresol, and benzothiazole/diphenyl ether. The quinoline/*m*-cresol and benzothiazole/*m*-cresol systems exhibit negative deviations from Raoult's law, due to acid–base attractions. All other systems show positive deviations from ideality. Common models for the excess Gibbs energy correlate the liquid-phase nonideality well. Vapor-phase nonideality is unimportant at the experimental conditions studied here.

Introduction

This study reports further results for vapor–liquid equilibria for model mixtures containing coal-derived liquids. These results contribute to a data base for chemical technology if coal is ever used, in lieu of petroleum, to produce liquid fuels or chemical feedstocks.

We report data at relatively high temperatures because such data are scarce and because there are no suitable model compounds for several structures prevalent in coal which can be studied below 150 °C.

Although many chemical processes operate at elevated temperatures, there are relatively few high-temperature vapor–liquid equilibrium data in the literature. For example, consider the DECHEMA (*1*) data compilation. In the four volumes devoted to mixtures containing an alkane and/or an aromatic, 1314 isotherms report data below 100 °C, 53 isotherms are in the range 100–150 °C, and only 9 isotherms are reported at temperatures above 150 °C.

To understand binary mixtures containing hydroaromatics, phenolics, aromatic amines, or aromatic ethers, we must obtain data at temperatures above 150 °C. There are no suitable model compounds with normal boiling points below 180 °C.

For the binary systems studied here, the model compounds are 1-methylnapthalene, *m*-cresol, quinoline, diphenyl ether, and tetralin. These represent structures commonly found in coal: aromatics, phenolics, heterocyclic nitrogen and sulfur compounds, ethers, and hydroaromatics. [Hydroaromatic compounds contain an aromatic ring fused with a saturated ring; the prototypical example is tetralin.] All of the compounds are bicyclic except *m*-cresol. All are aromatic except tetralin.

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Table I. Vapor–Liquid Equilibria for the System Quinoline (1)/1-Methylnaphthalene (2)

press., kPa	x_1	y_1	press., kPa	x_1	y_1
	180.4 °C		45.28	0.3949	0.3590^b
19.79	1.00	1.00	45.47	0.3265	0.2935
20.46	0.8882	0.8643	46.07	0.2526	0.2271
20.99	0.7786	0.7406	46.78	0.1578	0.1423^b
21.33	0.7004	0.6532^a	46.91	0.0849	0.0763^c
21.88	0.5941	0.5493	47.48	0.00	0.00
22.23	0.4913	0.4457			
22.62	0.4014	0.3631		230.3 °C	
22.74	0.3251	0.2924^a	73.59	1.00	1.00
23.10	0.2522	0.2267	75.57	0.8903	0.8664
23.47	0.1570	0.1432	77.64	0.7744	0.7368
23.69	0.0847	0.0755	78.68	0.7023	0.6607
23.85	0.00	0.00	80.39	0.6035	0.5609
			81.83	0.4950	0.4531
	205.3 °C		83.07	0.3975	0.3615
39.69	1.00	1.00	83.97	0.3272	0.2951
40.97	0.8863	0.8649	84.74	0.2550	0.2300
42.14	0.7772	0.7393^b	86.02	0.1584	0.1426^d
42.59	0.7055	0.6630	86.52	0.0854	0.0754
43.56	0.6001	0.5545	87.52	0.00	0.00
44.41	0.4946	0.4512			

^{a}180.3 °C. ^{b}205.4 °C. ^{c}205.2 °C. ^{d}230.4 °C.

Several obvious choices for model compounds are not included. The high melting points (above 40 °C) of naphthalene, phenol, and benzopyrrole (indole) make them unsuitable for our experimental apparatus. Benzothiophene (thionaphthene) and benzofuran (coumaron) are prohibitively expensive.

Structural groups found in coal include acidic and basic groups. Quinoline, benzothiazole (bases), and *m*-cresol (acid) represent such groups. *m*-Cresol is particularly interesting because deoxygenation of phenolic oxygen is more difficult than that for carbonyl, ether, or carboxylic-acid oxygen. Also, phenols can covert to furans under coal-liquefaction processing conditions (*2*). Oxygen must be removed from coal-derived liquids prior to use as engine fuels. [Sulfur, nitrogen, and oxygen can all poison reforming catalysts used to upgrade gasolines.]

Experimental Section

Benzothiazole, diphenyl ether, 1-methylnaphthalene, quinoline, and tetralin were supplied by Aldrich (nominal purities of 99, 99, 97, 96, and 99%, respectively); *m*-cresol was supplied by J. T. Baker (practical grade). All chemicals were purified by distillation under vacuum with a 15-tray Oldershaw column operating at a reflux ratio greater than 3.0. The final purity of all chemicals, as measured by gas chromatography, was greater than 99.8%. To prevent degradation of the chemicals, a small amount of triphenylphosphine (0.5 g/L was added to the systems containing quinoline or *m*-cresol.

Vapor–liquid equilibria and pure-component vapor pressures were measured by using a recirculating still. Vapor and liquid compositions were analyzed by gas chromatography. The experimental apparatus is described in the preceding paper of this series (*6*). No major modifications were necessary to use the still at high temperature.

All gas-chromatographic columns were 2.0 m long, containing 80/100-mesh packings supplied by Varian. The column-packing materials used were 15% FFAP/Chromosorb W-AW (quinoline/1-methylnaphthalene, quinoline/*m*-cresol, benzothiazole/*m*-cresol), 10% Carbowax 20M/Chromosorb W-HP (tetralin/*m*-cresol), and 3% OV-101/Chromosorb W-HP (benzothiazole/diphenyl ether).

All measurements, analyses, and transfer operations were vented to or completely enclosed within a fume hood. Particular care was exercised when *m*-cresol (very caustic), quinoline, or 1-methylnaphthalene (carcinogens) was used.

Table II. Vapor–Liquid Equilibria for the System Benzothiazole (1)/*m*-Cresol (2)

press., kPa	x_1	y_1	press., kPa	x_1	y_1
	160.3 °C		27.40	0.7329	0.6415
29.90	0.00	0.00	26.08	0.8136	0.7651^a
27.52	0.0919	0.0189	25.56	0.8989	0.8786
24.30	0.1994	0.0575	25.37	0.9356	0.9249
21.83	0.2981	0.1168	25.37	0.9530	0.9457
19.50	0.3837	0.1860	25.26	0.9864	0.9841
16.83	0.5176	0.3415	25.20	1.00	1.00
15.22	0.6293	0.5043			
14.07	0.7321	0.6609		200.3 °C	
13.60	0.8158	0.7816	97.96	1.00	1.00
13.51	0.8991	0.8884	90.79	0.0920	0.0235
13.40	0.9343	0.9322	82.30	0.1986	0.0653
13.49	0.9504	0.9510	74.05	0.3000	0.1265
13.48	0.9866	0.9857	67.73	0.3835	0.1914
13.41	1.00	1.00	58.76	0.5245	0.3382
			53.13	0.6329	0.4836
	180.3 °C		49.26	0.7342	0.6302
56.00	0.00	0.00	46.82	0.8175	0.7524
51.70	0.0916	0.0216	45.38	0.9004	0.8717
46.30	0.1984	0.0616	44.87	0.9360	0.9188
41.67	0.2987	0.1209	44.62	0.9524	0.9392
37.58	0.3830	0.1888^a	44.42	0.9866	0.9727
32.48	0.5237	0.3421	44.22	1.00	1.00
29.52	0.6314	0.4921			

^{a}180.2 °C.

Table III. Vapor–Liquid Equilibria for the System Quinoline (1)/*m*-Cresol (2)

press., kPa	x_1	y_1	press., kPa	x_1	y_1
	160.4 °C		22.32	0.7350	0.7179
29.79	0.00	0.00	22.63	0.8740	0.8995
26.79	0.1096	0.0079	23.14	0.9174	0.9475
22.33	0.2330	0.0334	23.57	1.00	1.00
16.39	0.3816	0.1513^a			
11.37	0.7470	0.7654		200.3 °C	
11.91	0.8735	0.9118	98.40	0.00	0.00
12.32	0.9178	0.9545	88.17	0.1057	0.0110
12.59	1.00	1.00	74.70	0.2418	0.0534
			58.49	0.3854	0.1717
	180.3 °C		41.06	0.7363	0.6960
55.96	0.00	0.00	40.57	0.8760	0.8851
50.01	0.1075	0.0084	40.79	0.9107	0.9243
42.30	0.2360	0.0402	41.81	1.00	1.00
32.52	0.3797	0.1535			

^{a}160.3 °C.

Results and Discussion

Tables I–V present experimental data. Three isotherms were measured for each of the five binary systems. To illustrate the results, Figure 1 shows data for the benzothiazole/diphenyl ether system at 194 and 214 °C.

The data were regressed to determine binary parameters for the Van Laar (*3*), NRTL (*4*), and UNIQUAC (*5*) models for the excess Gibbs energy. These binary parameters are given in Table VI. Details of the regression procedure are given in the preceding paper of this series (*6*).

The largest source of experimental error is composition measurement. With multiple sampling and multiple analyses, our composition uncertainty was usually less than 0.0015 mole fraction. Pressure measurements were accurate to ca. 0.05 kPa; temperature measurements were accurate to ca. 0.1 °C, except for the highest benzothiazole/diphenyl ether system (237 °C), where temperature stability was a problem; for this one isotherm, we estimate our temperature uncertainty to be 0.7 °C.

Vapor-phase nonidealities are small. Vapor-phase fugacity coefficients were calculated by the method of Hayden and O'Connell (*7*). All calculated vapor-phase fugacity coefficients

Table IV. Vapor-Liquid Equilibria for the System Diphenyl Ether (1)/Benzothiazole (2)

press., kPa	x_1	y_1	press., kPa	x_1	y_1
	194.2 °C		47.90	0.5932	0.4303
37.19	0.00	0.00	43.94	0.7279	0.5752
36.75	0.0432	0.0311[a]	41.50	0.8123	0.6761
36.16	0.0708	0.0466[a]	39.12	0.8846	0.7854
35.23	0.1248	0.0783	37.62	0.9384	0.8766
34.13	0.2086	0.1301	35.07	1.00	1.00
31.51	0.3882	0.2551			
29.89	0.4702	0.3138		237.1 °C	
27.83	0.5906	0.4210	108.36	0.00	0.00
25.41	0.7238	0.5638	107.06	0.0390	0.0290
23.83	0.8093	0.6645	105.12	0.0806	0.0554
22.39	0.8805	0.7731	102.07	0.1621	0.1058
21.52	0.9352	0.8662[a]	101.01	0.2117	0.1395
19.87	1.00	1.00	96.09	0.3497	0.2294
			90.63	0.4722	0.3246
	214.2 °C		84.36	0.5935	0.4306
62.91	0.00	0.00	78.32	0.7264	0.5797
62.37	0.0389	0.0269[b]	73.89	0.8173	0.6914
60.95	0.0794	0.0525	73.17	0.8281	0.7069[c]
59.20	0.1533	0.0987	67.22	0.9403	0.8834[c]
58.12	0.2099	0.1335	63.08	0.00	1.00
54.28	0.3679	0.2454			
51.70	0.4726	0.3189			

[a] 194.3 °C. [b] 214.3 °C. [c] 237.2 °C.

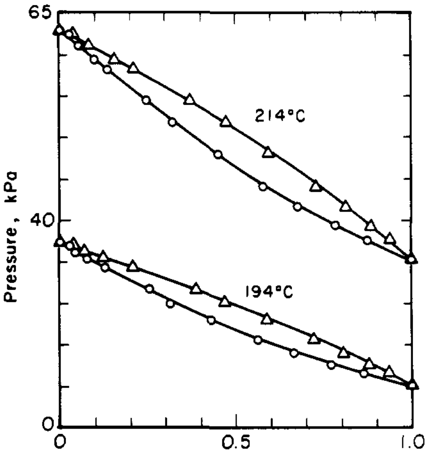

Figure 1. Vapor-liquid equilibria for the system benzothiazole/diphenyl ether.

are between 1.00 (ideal) and 0.94. Vapor-phase nonideality was generally unimportant for reducing data for correlation of liquid-phase nonideality. Binary parameters for models of the excess Gibbs energy, assuming ideal vapor-phase behavior, are given in the supplementary material.

The Poynting correction is very nearly unity for the experimental conditions of this study and can be neglected.

Two systems exhibit azeotropes. The tetralin/*m*-cresol system has maximum-pressure azeotropes of 0.545, 0.465, and 0.410 mole fraction tetralin at 150, 175, and 195 °C and 25.5, 54.4, and 93.1 kPa, respectively. The quinoline/*m*-cresol system has minimum-pressure azeotropes of 0.778, 0.810, and 0.837 mole fraction quinoline at 160, 180, and 200 °C and 11.3, 22.3, and 40.5 kPa, respectively.

Both the benzothiazole/*m*-cresol and quinoline/*m*-cresol systems show significant negative deviations from ideality, due to attraction betwen the acidic, hydroxyl hydrogen on the cresol and the basic, heterocyclic nitrogen in both quinoline and benzothiazole.

As measured by pK_a values, quinoline is a stronger base than benzothiazole. We therefore expect deviations from ideality to be more negative for the quinoline/*m*-cresol system than those for the benzothiazole/*m*-cresol system. For example, at 160 °C, the extrapolated infinite-dilution activity coefficients for the quinoline/*m*-cresol system are 0.15 (quinoline in *m*-cresol) and 0.19 (*m*-cresol in quinoline). At the same temperature, the extrapolated infinite-dilution activity coefficients for the benzothiazole/*m*-cresol system are 0.36 (benzothiazole in *m*-cresol) and 0.43 (*m*-cresol in benzothiazole). Figure 2 shows activity coefficients for the benzothiazole/*m*-cresol system.

Table V. Vapor-Liquid Equilibria for the System Tetralin (1)/*m*-Cresol (2)

press., kPa	x_1	y_1	press., kPa	x_1	y_1
	150.3 °C		54.14	0.5298	0.5122
21.66	1.00	1.00	54.14	0.5034	0.4924
23.08	0.9241	0.8755	54.41	0.4810	0.4753
23.80	0.8650	0.8026[a]	54.21	0.3500	0.3833
24.76	0.8077	0.7425	53.31	0.2719	0.3217
25.28	0.7395	0.6836[b]	53.05	0.2373	0.2917
24.95	0.7377	0.6819	52.23	0.1783	0.2365
25.46	0.6707	0.6319	51.48	0.1275	0.1815
25.36	0.6195	0.5957	50.68	0.0948	0.1411
25.44	0.5963	0.5809	49.83	0.0487	0.0774[d]
25.33	0.5705	0.5627	47.55	0.00	0.00
25.70	0.5529	0.5506[b]			
25.40	0.5269	0.5347[a]		195.3 °C	
25.49	0.5007	0.5163	76.09	1.00	1.00
25.39	0.4628	0.4906	83.19	0.8751	0.8080
25.10	0.3491	0.4112[a]	86.17	0.8130	0.7361
24.64	0.2730	0.3512[b]	88.46	0.7482	0.6727
24.63	0.2398	0.3211	90.02	0.6868	0.6168
23.70	0.1738	0.2568	90.12	0.6851	0.6168
23.40	0.1320	0.2084	92.08	0.5821	0.5382
22.86	0.0954	0.1607	91.78	0.5737	0.5291
22.10	0.0465	0.0843	91.89	0.5730	0.5266
21.12	0.00	0.00	91.81	0.5559	0.5162
			92.16	0.5432	0.5073
	175.3 °C		92.51	0.5084	0.4808
45.31	1.00	1.00	92.24	0.4835	0.4619[e]
47.74	0.9261	0.8792[c]	93.03	0.3516	0.3658
49.60	0.8722	0.8060	92.39	0.2729	0.3044
51.45	0.8091	0.7377	92.00	0.2410	0.2775
52.24	0.7459	0.6774[c]	90.81	0.1757	0.2155
53.09	0.6870	0.6278	89.87	0.1294	0.1694
53.31	0.6778	0.6208	88.81	0.0926	0.1271
53.49	0.6047	0.5664[c]	87.31	0.0480	0.0701
53.85	0.5732	0.5402[c]	84.49	0.00	0.00
53.81	0.5716	0.5437[c]			
53.80	0.5666	0.5387[c]			

[a] 150.2 °C. [b] 150.4 °C. [c] 175.2 °C. [d] 175.4 °C. [e] 195.2 °C.

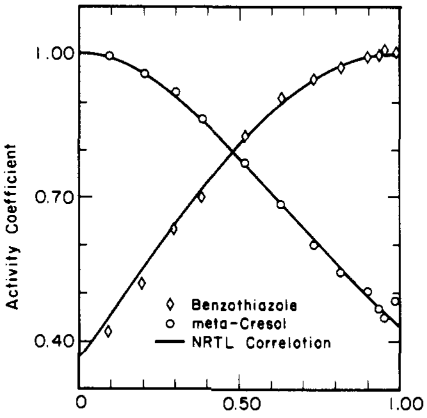

Figure 2. Activity coefficients for the system *m*-cresol/benzothiazole at 160 °C.

According to pK_a values, aniline is a stronger base than benzothiazole. However, our data for the aniline/*m*-cresol system (*8*) show smaller negative deviations from ideality than those for the benzothiazole/*m*-cresol system, probably because aniline's tendency to self-associate partially counteracts the

Table VI. Binary Parameters for the Van Laar, NRTL, and UNIQUAC Models for the Excess Gibbs Energy

temp, °C	model	$P(1)^a$	$P(2)^a$	root-mean-squared dev			
				P, kPa	T, °C	x	y
1-Methylnaphthalene (1)/Quinoline (2)							
180.4	UNIQUAC	119.0	−96.06	0.00	0.1	0.0011	0.0010
	NRTL	347.1	−246.3	0.00	0.1	0.0011	0.0010
	Van Laar	0.070	0.089	0.00	0.1	0.0011	0.0010
205.3	UNIQUAC	60.41	−47.87	0.00	0.1	0.0005	0.0008
	NRTL	57.23	8.49	0.00	0.1	0.0005	0.0008
	Van Laar	0.068	0.069	0.00	0.1	0.0005	0.0008
230.3	UNIQUAC	57.28	−46.14	0.00	0.0	0.0006	0.0004
	NRTL	34.00	23.85	0.00	0.0	0.0006	0.0004
	Van Laar	0.057	0.058	0.00	0.0	0.0006	0.0004
Benzothiazole (1)/*m*-Cresol (2)							
160.3	UNIQUAC	−217.5	73.14	0.01	0.1	0.0013	0.0013
	NRTL	−603.8	−122.4	0.01	0.1	0.0013	0.0014
	Van Laar	−1.003	−0.849	0.01	0.1	0.0013	0.0014
180.3	UNIQUAC	−185.1	41.91	0.00	0.1	0.0018	0.0015
	NRTL	−427.6	−232.6	0.00	0.1	0.0018	0.0015
	Van Laar	−0.803	−0.752	0.00	0.1	0.0018	0.0015
200.3	UNIQUAC	−166.8	30.21	0.00	0.1	0.0025	0.0034
	NRTL	−306.8	−277.1	0.00	0.1	0.0025	0.0034
	Van Laar	−0.653	−0.648	0.00	0.1	0.0025	0.0034
Quinoline (1)/*m*-Cresol (2)							
160.4	UNIQUAC	−162.5	−53.64	0.01	0.5	0.0048	0.0054
	NRTL	−845.9	−491.8	0.01	0.5	0.0052	0.0055
	Van Laar	−1.864	−1.648	0.01	0.5	0.0050	0.0055
180.3	UNIQUAC	−159.1	−38.34	0.01	0.2	0.0078	0.0047
	NRTL	−804.2	−411.9	0.01	0.2	0.0081	0.0047
	Van Laar	−1.609	1.409	0.01	0.2	0.0079	0.0047
200.3	UNIQUAC	−129.7	−53.57	0.00	0.2	0.0029	0.0051
	NRTL	−668.7	−443.7	0.00	0.2	0.0030	0.0052
	Van Laar	−1.343	−1.247	0.00	0.2	0.0030	0.0051
Diphenyl Ether (1)/Benzothiazole (2)							
194.2	UNIQUAC	37.09	−19.29	0.01	0.2	0.0020	0.0035
	NRTL	−418.1	664.2	0.01	0.2	0.0020	0.0035
	Van Laar	0.206	0.128	0.01	0.2	0.0020	0.0035
214.2	UNIQUAC	84.39	−62.00	0.00	0.2	0.0041	0.0069
	NRTL	−392.6	625.8	0.00	0.2	0.0041	0.0068
	Van Laar	0.190	0.129	0.00	0.2	0.0041	0.0069
237.1	UNIQUAC	−259.0	393.1	0.01	0.7	0.0030	0.0073
	NRTL	−968.0	1732.2	0.01	0.6	0.0033	0.0070
	Van Laar	0.266	0.120	0.01	0.7	0.0031	0.0072
Tetralin (1)/*m*-Cresol (2)							
150.3	UNIQUAC	216.1	−108.6	0.00	0.1	0.0020	0.0022
	NRTL	644.0	14.85	0.00	0.1	0.0020	0.0022
	Van Laar	0.625	0.783	0.00	0.1	0.0020	0.0022
175.3	UNIQUAC	138.1	−57.19	0.01	0.1	0.0013	0.0008
	NRTL	330.9	240.5	0.01	0.1	0.0013	0.0008
	Van Laar	0.600	0.619	0.01	0.1	0.0013	0.0008
195.3	UNIQUAC	120.2	−46.28	0.00	0.1	0.0006	0.0007
	NRTL	250.0	290.5	0.00	0.1	0.0005	0.0007
	Van Laar	0.559	0.552	0.00	0.1	0.0006	0.0007

[a] For the UNIQUAC and NRTL models, parameters $P(1)$ and $P(2)$ have dimensions calories/mole; for the Van Laar model, they are dimensionless.

aniline/cresol acid–base attraction. The infinite-dilution activity coefficients are 0.74 (aniline in *m*-cresol) and 0.80 (*m*-cresol in aniline) at 165 °C.

These strong acid–base interactions may be important for processing coal-derived liquids. In coal-liquefaction processes, separation operations may precede heteroatom-removal operations. (If coal is used to produce gasoline, sulfur, nitrogen, and oxygen must be removed.) Small molecules would be found in high-molecular-weight fractions if their activities are significantly reduced due to strong acid–base interactions.

In absence of specific interactions, the aromatic/aromatic systems show small positive deviations from ideality, as indicated in the previous paper (*6*) and as generally shown by aromatic/aromatic systems in the literature (*9*). [However, because of the high polarizability of aromatic molecules, if one substituent is highly polar, negative deviations can result due to induction effects.] While attractive interactions may cause significant negative deviations from ideality (as noted above), if one substituent is self-associating (e.g., phenol), large positive deviations can result.

The quinoline/1-methylnaphthalene system exhibits small deviations from ideality; all calculated activity coefficients are between 1.00 (ideal) and 1.10. All calculated activity coefficients for the benzothiazole/diphenyl ether system are between 1.35 and 0.99.

The tetralin/*m*-cresol system exhibits moderate positive deviations from ideality, as shown in Figure 3. At 150 °C, the extrapolated infinite-dilution activity coefficients are 1.87 (tetralin in *m*-cresol) and 2.22 (*m*-cresol in tetralin).

The large size of these molecules tends to decrease the magnitude of positive deviations from ideality. A given functional group on/in a single ring will have a larger effect than that of the same group on/in a bicyclic structure. For example, literature data for the pyridine/toluene system (*1*) indicate larger

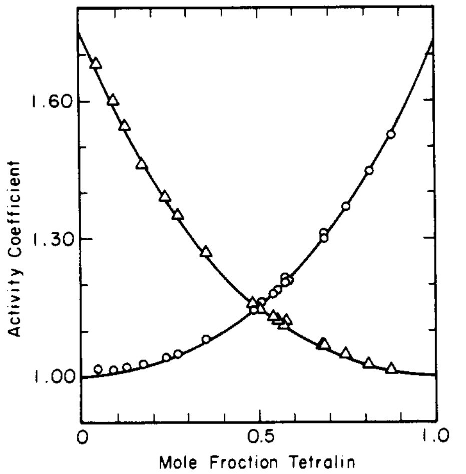

Figure 3. Activity coefficients for the system *m*-cresol/tetralin at 150 °C.

positive deviations from ideality than those found for the quinoline (benzopyridine)/1-methylnaphthalene (benzotoluene) system.

For the systems studied here, correlation of experimental data with models for the excess Gibbs energy is good. Table VI lists mean deviations between experimental and calculated pressures, temperatures, and compositions for all isotherms. For all systems, there are no significant differences in the quality of correlation amongst the Van Laar, NRTL, and UNIQUAC models for the excess Gibbs energy.

The correlations for the tetralin/*m*-cresol, benzothiazole/*m*-cresol, and quinoline/1-methylnaphthalene systems generally agree with the data to within experimental uncertainty.

The two-parameter NRTL, UNIQUAC, and Van Laar models do not correlate the quinoline/*m*-cresol data to whith our estimated experimental uncertainty. Nevertheless, the data for this system appear thermodynamically consistent according to the criteria of Christiansen and Fredenslund (*10*) and Herington (*11*). Of the ten binary systems measured in this study, this system exhibits the most significant deviations from ideality.

The benzothiazole/diphenyl ether data appear less reliable. For example, the data at 150 °C satisfy the Herington criterion within 19% (2–10% is usually considered acceptable).

Registry No. Quinoline, 91-22-5; 1-methylnaphthalene, 90-12-0; *m*-cresol, 1319-77-3; tetralin, 119-64-2; benzothiazole, 95-16-9; diphenyl ether, 101-84-8.

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Supplementary Material Available: Parameters for excess-Gibbs-energy models for the binary systems quinoline/1-methylnaphthalene, quinoline/*m*-cresol, tetralin/*m*-cresol, benzothiazole/*m*-cresol, and benzothiazole/diphenyl ether (2 pages). Ordering information is given on any current masthead.

Vapor–Liquid Equilibria for Model Mixtures of Coal-Derived Liquids. 3. Ternary Systems with Benzene, Cyclohexane, and a Heterocycle

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Vapor–liquid equilibria were measured for four ternary systems: benzene/cyclohexane/heterocycle where the heterocycle is thiophene, 2-methylfuran, pyridine, or pyrrole. These systems are models for the behavior of heterocyclic structures in coal-derived liquids of varying aromatic content. All systems show positive deviations from ideality. In ascending order, the relative magnitude of activity coefficients due to heteroatoms is oxygen, sulfur, nitrogen (basic), nitrogen (nonbasic). The ternary experimental data are satisfactorily represented by a model for the excess Gibbs energy using adjustable parameters determined from binary data only. The quality of ternary correlation is directly related to the quality of the binary data used to determine model parameters.

Introduction

This study reports vapor–liquid equilibria for ternary mixtures containing benzene, cyclohexane, and a heterocycle. Our motivation is to obtain fundamental data for the thermodynamic activities of heterocycles in coal-derived liquids of varying aromatic content.

The chemical composition of coal is more diverse than that of petroleum. The relative amounts of constituent elements (primarily carbon, hydrogen, oxygen, nitrogen, and sulfur) and functional groups vary appreciably depending upon the rank, maceral class, and source of the coal (*1*).

The atomic hydrogen:carbon (H:C) ratio in a coal usually ranges between 0.8 and 0.9, although some coals have H:C ratios as high as 1.0. (Higher H:C ratios usually enhance the economics of coal liquefaction; hydrogen addition is a major expense in the overall liquefaction process.) The H:C ratio is not significantly changed during direct liquefaction.

The aromaticity of coal varies significantly with rank and maceral class. The aromatic content of bituminous coal may range between 50 and 90%. At high dilution, the activity coefficient of a heteroatomic component (containing oxygen, nitrogen, or sulfur) changes significantly with the aromaticity of a mixture.

To quantify this change, we chose a ternary model system to study how vapor–liquid equilibria (VLE) change with aro-

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