

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 within our es-

timated 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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maticity. The model system is benzene, cyclohexane, and a heterocycle. The heterocycles are thiophene, 2-methylfuran, pyridine (basic nitrogen), and pyrrole (nonbasic nitrogen).

There are no VLE data in the literature for ternary systems with thiophene, 2-methylfuran, or pyrrole. There is only a single datum for the pyridine/benzene/cyclohexane system (2).

To determine the effect of mixture aromaticity on activity coefficients of heterocyclic components in a coal-derived liquid, we limited experimental effort to the ternary concentration range where aromaticity levels are typical of those found in coal-derived liquids.

VLE data for the binary systems benzene/cyclohexane, benzene/pyridine, cyclohexane/pyridine, benzene/thiophene, and cyclohexane/thiophene are in the literature (3), although data for the latter two systems are limited. In the first paper of this series (4), we reported VLE data for the binary systems 2-methylfuran/benzene and 2-methylfuran/cyclohexane. We are not aware of any VLE data for any binary system including pyrrole.

### Experimental Section

The chemicals are all commercially available. Benzene, cyclohexane (both spectrophotometric grade, Mallinckrodt), pyridine (glass distilled, OmniSolv/MCB), and thiophene (gold label spectrophotometric, Aldrich) were not purified further. Pyrrole and 2-methylfuran (both 99%, Aldrich) were distilled under vacuum in a 15-tray Oldershaw column at a reflux ratio greater than 3.0. As measured by gas chromatography (GC), the final purity of each chemical was greater than 99.9%, except for pyrrole (99.8%).

Pyrrole is easily oxidized and was blanketed with nitrogen at all times (during distillation and VLE measurements). All VLE measurements for pyrrole-containing systems were done immediately following purification.

Both pure-component vapor pressures and vapor-liquid equilibria were measured with a recirculating still. Vapor and liquid compositions were analyzed by GC. The experimental apparatus was described previously (4).

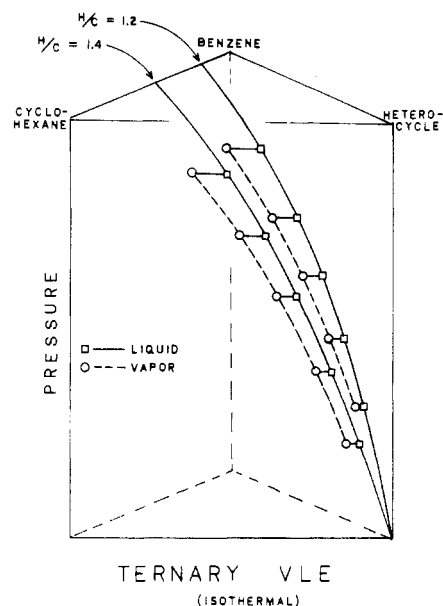
The GC columns used for composition analysis were 15% FFAP/Chromosorb AW (3.0 m for the 2-methylfuran system; 2.0 m for the thiophene system) and 10% Carbowax 20M with 5% KOH/Chromosorb W-HP (2.0 m for the pyridine and pyrrole systems), supplied by Varian. All column packings were 80/100 mesh.

The GC was calibrated with gravimetrically prepared standard mixtures. For each system, at least 18 calibration standards were prepared, covering the range of experimental interest. At least four GC analyses were made of each calibration standard. The average standard deviation for analysis of the standards was less than 0.001 mole fraction.

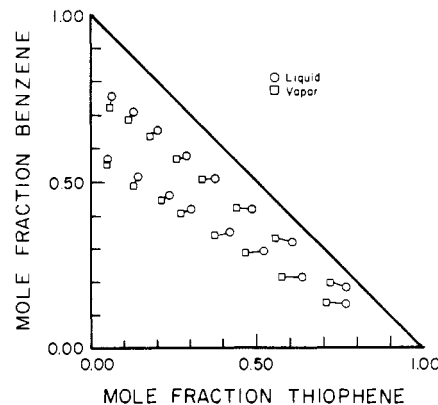
All GC peaks were well-separated with minimal tailing. At least two analyses were made of each vapor and liquid composition.

For the pyrrole system, any GC column packing capable of separating benzene and cyclohexane retains pyrrole longer than desirable. For the pyrrole system (only), two composition analyses were "piggy-backed", so as to reduce (by almost half) the time necessary for composition analyses. A vapor sample is injected while the liquid sample was still eluting; then the analysis would be repeated, this time with the vapor sample injected first. The order of elution was cyclohexane (first injection), benzene (first injection), cyclohexane (second injection), benzene (second injection), pyrrole (first injection), pyrrole (second injection). There was no significant loss of reproducibility for these analyses.

To concentrate our effort on aromaticity levels typical of coal-derived liquids, the molar benzene:cyclohexane ratio in the liquid was maintained at either approximately 4:1 (80% aro-



**Figure 1.** Schematic representation of isothermal vapor-liquid equilibrium data for a ternary system; two pseudobinary isotherms are shown, each having a constant benzene:cyclohexane ratio in the liquid phase.



**Figure 2.** Vapor-liquid equilibria for the thiophene/benzene/cyclohexane system at 80.8 °C; the diagram is a two-dimensional projection of the data onto an isobaric plane.

matic; H:C = 1.2) or 3:2 (80% aromatic; H:C = 1.4). As illustrated in Figure 1, in essence, two pseudobinary systems were studied: heterocycle with a 4:1 benzene:cyclohexane mixture, and heterocycle with a 3:2 benzene/cyclohexane mixture.

Caution must always be maintained when working with benzene (carcinogenic), pyridine, and thiophene (stench). All experimental work was either directly vented to or completely enclosed within a fume hood.

### Results

Experimental data are listed in Tables I-IV. One isotherm was measured for the pyrrole system. Two isotherms were measured for each of the other systems.

Figure 2 shows data for the thiophene/benzene/cyclohexane system at 65 °C. Each tie line in Figure 2 shows a vapor-liquid equilibrium datum at the saturation pressure and 65 °C. Since saturation pressure is a unique function of temperature at fixed composition, each tie line is at a different pressure. Figure 2 is the projection onto a constant-pressure plane of the type of data indicated in Figure 1.

Pressure measurements are accurate to 0.04 kPa. Temperature measurements are accurate to 0.1 °C. Our estimated

**Table I. Ternary Vapor (y)-Liquid (x) Equilibria for the System 2-Methylfuran (1)/Benzene (2)/Cyclohexane (3)**

press., kPa	mole fractions			
	$x_1$	$y_1$	$x_2$	$y_2$
45.7 °C				
33.88	0.025	0.040	0.793	0.736
34.36	0.049	0.080	0.767	0.700
35.29	0.032	0.054	0.579	0.544
35.50	0.095	0.150	0.735	0.648
36.81	0.090	0.148	0.546	0.487
38.20	0.213	0.307	0.641	0.527
38.96	0.181	0.270	0.508	0.411
39.34	0.269	0.377	0.596	0.473
39.78	0.208	0.304	0.475	0.389
40.95	0.263	0.366	0.444	0.352
41.74	0.378	0.494	0.506	0.380
43.47	0.382	0.494	0.372	0.274
44.38	0.507	0.617	0.401	0.284
45.93	0.508	0.603	0.295	0.208
48.68	0.731	0.802	0.215	0.142
48.81	0.666	0.741	0.196	0.128
51.78	0.861	0.891	0.080	0.050
53.58	1.00	1.00	0.00	0.00
30.68	0.00	0.00	1.00	1.00
30.85	0.00	0.00	0.00	0.00
65.8 °C				
68.85	0.023	0.038	0.795	0.746 <sup>a</sup>
70.07	0.046	0.073	0.775	0.717
71.49	0.030	0.051	0.582	0.551
72.58	0.100	0.155	0.733	0.655
74.23	0.085	0.137	0.551	0.500
77.29	0.207	0.300	0.647	0.540
78.53	0.176	0.261	0.496	0.423
79.67	0.263	0.368	0.602	0.486
82.33	0.260	0.364	0.446	0.359
84.22	0.373	0.488	0.511	0.391
87.20	0.376	0.487	0.376	0.283
89.39	0.500	0.610	0.406	0.295
92.28	0.505	0.607	0.297	0.211
97.80	0.657	0.737	0.203	0.135
98.07	0.728	0.801	0.218	0.146
104.11	0.861	0.891	0.080	0.052
107.89	1.00	1.00	0.00	0.00
63.84	0.00	0.00	1.00	1.00
63.17	0.00	0.00	0.00	0.00

<sup>a</sup> Temperature = 65.7 °C.

composition uncertainty is 0.004 mole fraction.

The largest source of experimental uncertainty is composition analysis. Standard deviations of composition measurements were usually less than 0.001 mole fraction. However, translation of composition data from relative GC response to mole fractions may cause systematic error. GC response factors are nonlinear across a large composition range.

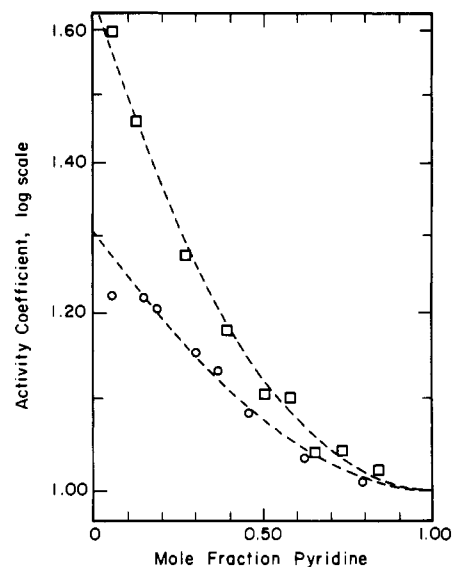
For each component  $i$ , the activity coefficient is calculated by

$$\gamma_i = \frac{y_i P}{x_i P_i^{\text{sat}}} \quad (1)$$

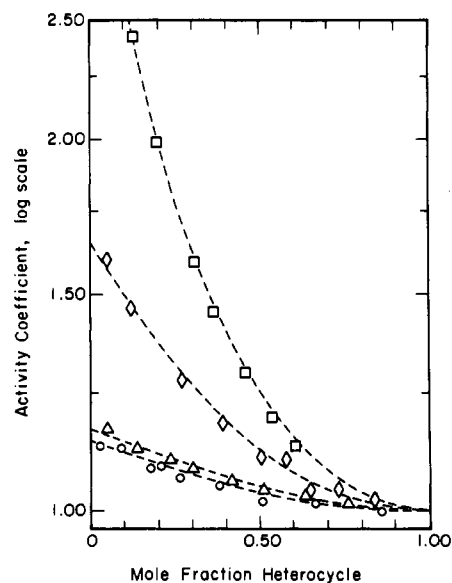
where  $y$  is the vapor-phase mole fraction,  $P$  is the pressure,  $x$  is the liquid-phase mole fraction, and  $P^{\text{sat}}$  is the pure-component saturation pressure.

For the conditions studied here, vapor-phase nonidealities are unimportant. Likewise, the Poynting correction can be neglected.

For all systems, deviations from Raoult's law are positive. For all systems, the activity coefficient of the heterocycle increases as the aromaticity of the mixture decreases. Activity coefficients decrease slightly with increasing temperature, but a small change in temperature has a minor effect compared with that due to a small change in composition.



**Figure 3.** Activity coefficients for pyridine in the benzene/cyclohexane/pyridine system at 60.8 °C: □, benzene:cyclohexane = 3:2; ○, benzene:cyclohexane = 4:1; ---, Wilson equation.



**Figure 4.** Activity coefficients for various heterocycles in a liquid mixture with benzene:cyclohexane ratio = 3:2: □, pyrrole at 81 °C; ◇, pyridine at 61 °C; △, thiophene at 61 °C; ○, 2-methylfuran at 46 °C; ---, Wilson equation.

Figure 3 shows activity coefficients for pyridine in the pyridine/benzene/cyclohexane system at 61 °C. The pyridine activity coefficient is higher when the benzene:cyclohexane ratio is lower.

Both thiophene and 2-methylfuran show very small deviations from ideality in the mixtures studied (60–80% aromatic). All calculated activity coefficients for these two heterocycles are between 1.00 (ideal) and 1.20.

In a model coal-derived liquid, the relative magnitude of the effect of the heteroatom on the activity coefficient of the heterocycle is

$$\gamma_{\text{nitrogen(nonbasic)}} > \gamma_{\text{nitrogen(basic)}} > \gamma_{\text{sulfur}} > \gamma_{\text{oxygen}}$$

This effect is shown in Figure 4.

The high nonideality of the nonbasic nitrogen heterocycle (pyrrole) is noteworthy. Activity coefficients are as high as 2.5. There are no pyrrole data in the literature for comparison, although limited data have been reported for binary systems with indole (5).

**Table II. Ternary Vapor (y)-Liquid (x) Equilibria for the System Thiophene (1)/Benzene (2)/Cyclohexane (3)**

press., kPa	mole fractions				
	$x_1$	$y_1$	$x_2$	$y_2$	
60.8 °C					
50.55	0.763	0.709	0.188	0.202	
52.24	0.763	0.691	0.136	0.141	
52.38	0.601	0.542	0.322	0.333	
53.48	0.484	0.430	0.419	0.423	
54.18	0.633	0.561	0.216	0.216	
54.51	0.371	0.327	0.512	0.506	
55.28	0.285	0.249	0.580	0.568	
55.29	0.514	0.451	0.293	0.287	
55.92	0.197	0.171	0.652	0.632	
56.18	0.417	0.367	0.351	0.340	
56.44	0.127	0.111	0.708	0.680	
56.97	0.064	0.055	0.757	0.725	
57.30	0.303	0.267	0.420	0.404	
57.81	0.235	0.208	0.460	0.442	
58.52	0.141	0.126	0.515	0.496	
59.05	0.051	0.047	0.568	0.551	
46.76	1.00	1.00	0.00	0.00	(thiophene)
53.71	0.00	0.00	1.00	1.00	(benzene)
53.31	0.00	0.00	0.00	0.00	(cyclohexane)
79.9 °C					
95.16	0.765	0.718	0.186	0.199	
97.72	0.766	0.706	0.135	0.140	
98.16	0.603	0.552	0.322	0.333	
100.19	0.484	0.438	0.419	0.423	
100.76	0.634	0.573	0.216	0.218	
101.76	0.374	0.334	0.511	0.509	
102.71	0.518	0.465	0.294	0.290	
103.00	0.288	0.257	0.579	0.570	
104.07	0.200	0.177	0.653	0.638	
104.37	0.417	0.373	0.351	0.343	
104.92	0.128	0.113	0.709	0.688	
105.81	0.064	0.056	0.757	0.722	
106.16	0.303	0.272	0.420	0.408	
106.98	0.235	0.213	0.460	0.446	
107.92	0.141	0.130	0.516	0.490	
108.05	0.050	0.049	0.568	0.556 <sup>a</sup>	
89.34	1.00	1.00	0.00	0.00	
100.80	0.00	0.00	1.00	1.00	
98.95	0.00	0.00	0.00	0.00	

<sup>a</sup>Temperature = 79.6 °C.**Correlation of Experimental Data**

Another motivation for measuring ternary VLE data is that such data are useful for testing the ability of models for the excess Gibbs energy to correlate multicomponent data. A useful assumption of models for the excess Gibbs energy is that only experimental binary data are needed to estimate multicomponent activity coefficients. Interactions in multicomponent systems are considered to be the sum of all possible binary interactions. Therefore, ternary (and higher-order) data should be superfluous. We wish to learn whether this is true for model mixtures for coal-derived liquids.

In addition to those calculated directly from experimental data, activity coefficients were also calculated from the Wilson model ( $\delta$ ) for the excess Gibbs energy. For multicomponent systems, the Wilson equation is

$$\ln \gamma_i = 1 - \ln \left( \sum_{j=1}^m x_j A_{ij} \right) - \sum_{k=1}^m \frac{x_k A_{ki}}{\sum_{j=1}^m x_j A_{kj}} \quad (2)$$

where

$$A_{ij} = A_{ji} = 1.0; \quad A_{ij} = \frac{v_j}{v_i} \exp(-a_{ij}/RT)$$

 $v$  is the pure-component liquid molar volume,  $a$  is the adjustable**Table III. Ternary Vapor (y)-Liquid (x) Equilibria for the System Pyridine (1)/Benzene (2)/Cyclohexane (3)**

press., kPa	mole fractions				
	$x_1$	$y_1$	$x_2$	$y_2$	
60.8 °C					
27.57	0.843	0.480	0.096	0.205	
27.71	0.793	0.444	0.168	0.356	
33.70	0.737	0.350	0.163	0.280	
35.70	0.621	0.277	0.309	0.486 <sup>a</sup>	
37.55	0.654	0.279	0.217	0.325	
40.63	0.582	0.242	0.263	0.357	
41.88	0.456	0.182	0.446	0.581	
43.42	0.505	0.198	0.310	0.389	
45.04	0.367	0.142	0.518	0.620	
47.37	0.393	0.150	0.370	0.422	
47.44	0.301	0.112	0.571	0.649	
51.04	0.273	0.105	0.443	0.469	
51.29	0.187	0.068	0.663	0.697	
52.57	0.148	0.053	0.694	0.712	
55.51	0.122	0.049	0.530	0.529	
55.63	0.051	0.017	0.770	0.752	
57.43	0.052	0.022	0.570	0.559	
15.39	1.00	1.00	0.00	0.00	(pyridine)
53.71	0.00	0.00	1.00	1.00	(benzene)
53.31	0.00	0.00	0.00	0.00	(cyclohexane)
80.8 °C					
54.58	0.844	0.519	0.096	0.201 <sup>b</sup>	
54.92	0.796	0.481	0.166	0.344	
65.36	0.736	0.378	0.163	0.278	
69.10	0.627	0.305	0.303	0.478	
77.98	0.580	0.260	0.263	0.360	
80.68	0.463	0.204	0.442	0.577	
82.89	0.511	0.221	0.306	0.391	
86.62	0.374	0.157	0.514	0.621	
90.32	0.396	0.168	0.369	0.426	
90.95	0.307	0.126	0.568	0.652	
96.40	0.288	0.121	0.439	0.475	
97.60	0.199	0.082	0.658	0.700	
100.44	0.154	0.062	0.691	0.717	
105.10	0.126	0.057	0.528	0.533	
106.04	0.055	0.021	0.771	0.761	
109.7	0.050	0.024	0.569	0.564 <sup>c</sup>	
33.52	1.00	1.00	0.00	0.00	
103.67	0.00	0.00	1.00	1.00	
101.71	0.00	0.00	0.00	0.00	

<sup>a</sup>Temperature = 60.7 °C. <sup>b</sup>Temperature = 80.9 °C. <sup>c</sup>Pressure estimated.**Table IV. Ternary Vapor (y)-Liquid (x) Equilibria for the System Pyrrole (1)/Benzene (2)/Cyclohexane (3) at 80.3 °C**

press., kPa	mole fractions				
	$x_1$	$y_1$	$x_2$	$y_2$	
81.86	0.541	0.145	0.369	0.572	
84.66	0.607	0.152	0.234	0.361	
87.46	0.447	0.121	0.448	0.613	
88.96	0.538	0.136	0.280	0.393	
92.91	0.346	0.100	0.530	0.646	
93.02	0.458	0.120	0.329	0.420	
96.81	0.261	0.081	0.598	0.673	
97.24	0.365	0.103	0.386	0.448	
99.46	0.306	0.093	0.420	0.465	
99.63	0.204	0.068	0.643	0.690	
103.09	0.136	0.050	0.701	0.718	
103.74	0.198	0.072	0.488	0.503	
107.00	0.125	0.053	0.525	0.526	
18.90	1.00	1.00	0.00	0.00	(pyrrole)
103.67	0.00	0.00	1.00	1.00	(benzene)
101.71	0.00	0.00	0.00	0.00	(cyclohexane)

binary parameter,  $R$  is the universal gas constant, and  $T$  is the temperature (absolute).

Two sets of binary parameters for the Wilson equation were determined. One set of parameters was determined from data in the literature for each of the possible binary systems.

**Table V. Activity Coefficients Calculated from Experimental Data and by the Wilson Equation for the System Pyridine (1)/Benzene (2)/Cyclohexane (3) at 60.8 °C**

press., kPa	calcd from Wilson parameters determined from								
	calcd from exptl ternary data			calcd from Wilson parameters determined from					
	$\gamma_1$	$\gamma_2$	$\gamma_3$	ternary data			binary data		
27.57	1.02	1.10	2.63	1.01	1.10	2.67	1.01	1.12	2.34
27.71	1.01	1.09	2.65	1.01	1.10	2.60	1.01	1.12	2.34
33.70	1.04	1.08	2.33	1.03	1.05	2.35	1.03	1.09	2.09
35.70	1.03	1.05	2.24	1.05	1.04	2.19	1.04	1.07	2.02
37.55	1.04	1.05	2.16	1.06	1.03	2.14	1.05	1.07	1.93
40.63	1.10	1.03	1.96	1.08	1.01	1.97	1.07	1.05	1.79
41.88	1.08	1.02	1.91	1.09	1.02	1.90	1.08	1.04	1.77
43.42	1.10	1.02	1.82	1.12	1.00	1.82	1.10	1.04	1.67
45.04	1.13	1.00	1.75	1.12	1.01	1.76	1.12	1.03	1.66
47.37	1.18	1.01	1.60	1.19	0.99	1.61	1.17	1.03	1.50
47.44	1.15	1.00	1.66	1.15	1.01	1.67	1.16	1.02	1.58
51.04	1.27	1.01	1.44	1.29	1.00	1.43	1.27	1.03	1.36
51.29	1.21	1.00	1.51	1.20	1.01	1.53	1.23	1.01	1.46
52.57	1.22	1.01	1.46	1.22	1.01	1.48	1.27	1.01	1.42
55.51	1.46	1.03	1.26	1.46	1.04	1.24	1.45	1.04	1.23
55.63	1.22	1.01	1.35	1.27	1.02	1.38	1.38	1.01	1.34
57.43	1.60	1.05	1.19	1.57	1.08	1.17	1.58	1.06	1.18

**Table VI. Average Deviations (percent) of Activity Coefficients Calculated with the Wilson Equation from Those Calculated from Experimental Data**

temp, °C	parameters determined from					
	ternary data			binary data		
	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_1$	$\gamma_2$	$\gamma_3$
Pyridine (1)/Benzene (2)/Cyclohexane (3)						
60.8	1.1	1.1	1.0	1.8	1.6	6.5
80.8	1.9	1.3	1.4	2.9	1.3	4.4
Thiophene (1)/Benzene (2)/Cyclohexane (3)						
60.8	0.5	0.5	0.6	2.8	1.2	1.7
79.9	2.4	1.6	1.2	3.5	1.5	0.6
2-Methylfuran (1)/Benzene (2)/Cyclohexane (3)						
45.7	0.8	1.8	1.1	0.9	1.9	1.0
65.8	0.7	1.0	0.5	0.5	1.0	0.8
Pyrrole (1)/Benzene (2)/Cyclohexane (3)						
80.8	1.0	0.4	0.6			

(However, no data are available for the benzene/pyrrole or cyclohexane/pyrrole systems.) The second set was determined from regression of our ternary data by Kolbe (7) using the regression technique described by Gmehling and Onken (8). The regression procedure uses the sum of the squared deviations of activity coefficients as the objective (minimization) function.

$$\sum_n \sum_i (\Delta\gamma_{i,n})^2 = \sum_n \sum_i \left( \frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}} \right)^2 \quad (3)$$

where  $n$  is the data point and  $i$  is the component.

Table V shows three sets of activity coefficients for the pyridine/benzene/cyclohexane system at 60.8 °C. The activity coefficients are calculated from (a) the experimental data; (b) the Wilson equation, using adjustable binary parameters determined by regression of the ternary experimental data; and (c) the Wilson equation, using adjustable binary parameters determined from regression of binary data in the literature.

Table VI shows average deviations (per cent) between activity coefficients calculated from ternary experimental data and those calculated according to the Wilson correlation. Two sets of deviations are listed: the first is the deviations between experimental data and correlations calculated from the ternary data; the second is the deviations between experiment and correlations determined from binary data in the literature (9–15).

**Table VII. Wilson Equation Parameters<sup>a</sup>**

	parameters determined from						temp, °C
	ternary data			binary data			
	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_1$	$\gamma_2$	$\gamma_3$	
Pyridine (1)/Benzene (2)/Cyclohexane (3)							
1.0	1.027	0.203	1.0	0.584	0.507		
60.8	0.809	1.0	1.403	1.274	1.0	0.913	
80.8	0.672	0.361	1.0	0.578	0.718	1.0	
	1.0	0.762	0.465	1.0	0.606	0.535	
	1.133	1.0	1.146	1.250	1.0	0.975	
	0.585	0.563	1.0	0.586	0.700	1.0	
2-Methylfuran (1)/Benzene (2)/Cyclohexane (3)							
1.0	1.030	0.859	1.0	0.470	0.619		
45.7	0.940	1.0	0.851	1.693	1.0	0.907	
	0.641	0.714	1.0	0.852	0.675	1.0	
	1.0	0.879	0.933	1.0	0.692	0.701	
	1.086	1.0	0.807	1.330	1.0	0.917	
	0.627	0.814	1.0	0.841	0.720	1.0	
Thiophene (1)/Benzene (2)/Cyclohexane (3)							
1.0	1.207	0.878	1.0	1.447	0.877		
60.8	0.793	1.0	0.920	0.551	1.0	0.913	
	0.581	0.709	1.0	0.571	0.718	1.0	
	1.0	1.088	1.010	1.0	1.427	0.899	
	0.832	1.0	0.786	0.566	1.0	0.975	
	0.542	0.855	1.0	0.579	0.699	1.0	
Pyrrole (1)/Benzene (2)/Cyclohexane (3)							
1.0	0.388	0.171					
80.8	1.038	1.0	0.914				
	0.394	0.767	1.0				

<sup>a</sup>Parameters are listed as shown here:

$$A_{11} \quad A_{12} \quad A_{13} \\ A_{21} \quad A_{22} \quad A_{23} \\ A_{31} \quad A_{32} \quad A_{33}$$

(See eq 2 for definition of  $A_{ij}$ .)

There is excellent agreement between activity coefficients calculated from the data with those calculated on the basis of model parameters determined by regression of the data. Agreement is also good with activity coefficients calculated by using parameters determined from binary data in the literature.

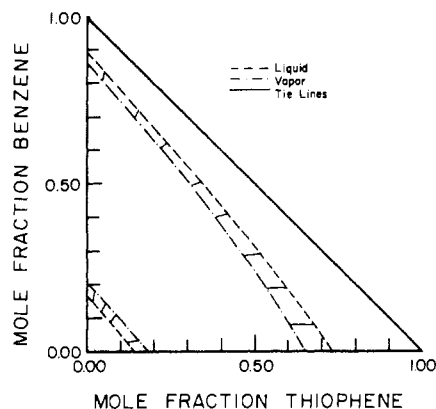
The results in Table VI indicate that for the mixtures studied here, multicomponent data are superfluous for correlating VLE. Table VII gives Wilson parameters.

## Discussion

Although direct correlation of the ternary data appears to give better results than that based upon binary data, such success is qualified. Parameters calculated directly from multicomponent data are frequently applicable only to the composition range studied.

For example, when the "ternary" parameters at 61 °C are used, the calculated infinite-dilution activity coefficient of benzene in an equimolar mixture of pyridine and cyclohexane is 0.84 (indicating negative deviations from Raoult's law). This is incorrect. Further, the ternary parameters lead to a calculated infinite-dilution activity coefficient of pyridine in cyclohexane of 6.8, an error of more than 100% (13). While the ternary parameters correlate the experimental data very well, they are unlikely to be useful for estimating liquid nonideality for compositions outside the range of experimental study.

Tamir and Wisniak have examined several ternary and quaternary systems (16, 17). Tamir (18) contends that "direct correlation" of multicomponent data results in better correlation of the data than if both multicomponent and binary data are used. By direct correlation we mean that only data corresponding to the mixture of highest order are used to determine model parameters.



**Figure 5.** Calculated vapor-liquid equilibria for the cyclohexane/benzene/thiophene system at 347.1 K and 1.050 bar.

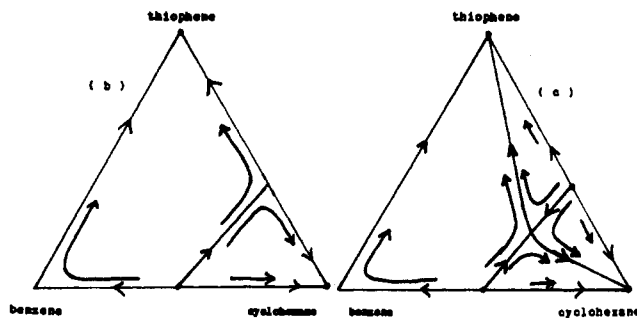
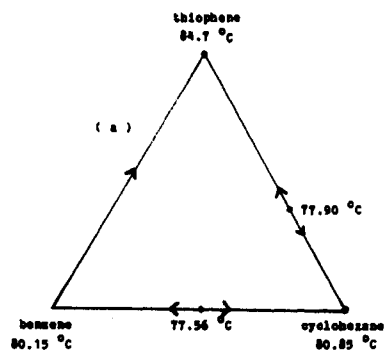
While these experiments support Tamir's contention, they also remind us that multicomponent data may often be satisfactorily estimated on the basis of parameters determined from binary data only. In that event, the experimental effort necessary to produce model parameters for a multicomponent system is much decreased. The ability to estimate multicomponent VLE behavior on the basis of binary data alone is a prime attribute of models for the excess Gibbs energy.

The quality of multicomponent-system correlation using model parameters determined from binary data only depends upon the quality of the binary data. For example, Table VI shows no qualitative difference between the two different sets of model parameters in correlating the 2-methylfuran/benzene/cyclohexane system. The three sets of binary data used to calculate model parameters for this ternary system are all thermodynamically consistent at a temperature close to that for the experimental ternary data.

It is encouraging that estimates for the ternary behavior of the systems containing pyridine and thiophene (using model parameters determined from binary data only) are relatively good. There are no thermodynamically consistent data for the pyridine/benzene system in the literature. There are no VLE data for the thiophene/cyclohexane system in the literature. (Model parameters were determined from  $P, T, x$  data measured at 45 °C.)

Once parameters for a model for the excess Gibbs energy are determined, a simple calculation determines how VLE behavior changes with pressure, temperature and/or composition. Figure 5 shows vapor-liquid equilibria for the thiophene/benzene/cyclohexane system at 80 °C and 105 kPa. Because of azeotropes in the constituent binary systems, two phase envelopes can exist at constant temperature and at pressures between the thiophene saturation pressure and the benzene/cyclohexane azeotropic pressure. The 2-methylfuran/benzene/cyclohexane system can also show two phase envelopes, at pressures between the benzene/cyclohexane azeotropic pressure and the pure-component saturation pressure of benzene.

There are no ternary azeotropes among the systems studied. However, the thiophene/benzene/cyclohexane system is interesting because two of the constituent binary systems (benzene/cyclohexane and thiophene/cyclohexane) have azeotropes. According to topological arguments of Doherty et al. (19, 20, 21) two qualitatively different types of behavior are possible for the thiophene/benzene/cyclohexane system; these are shown by the residue curve maps in Figure 6. (These plots show the change in liquid composition at constant pressure for a Rayleigh distillation.) Depending upon the initial liquid composition, the last liquid residue distilled is either pure thiophene or pure cyclohexane. Analysis of the ternary data indicate that the behavior shown in Figure 6c is qualitatively correct.



**Figure 6.** Residue curve maps for the system thiophene/benzene/cyclohexane: 101.3 kPa (1.0 atm) isobar: (a) pure-component boiling points and binary azeotrope temperatures; (b) possible residue curve map with no ternary azeotrope; (c) possible residue curve map with ternary saddle point.

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**Registry No.** Thiophene, 110-02-1; 2-methylfuran, 534-22-5; pyridine, 110-86-1; pyrrole, 109-97-7; benzene, 71-43-2; cyclohexane, 110-82-7.

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