Table III. Temperature Dependence of Pitzer Coefficients for Aqueous $SrCl_2$ at 20.27 bar and from 50 to 200 °C Using Eq 6

Pitzer coeff	10^2q_0	10^4q_1	10^6q_2	10^9q_3	$10^5\sigma$
$(\partial\beta^0/\partial P)_T$	0.8056	−0.6303	0.1645	−0.1425	0.81
$(\partial C^\phi/\partial P)_T$	0.2607	−0.2027	0.0508		0.05

$\phi_V{}^0$ is the partial molal volume at infinite dilution. A_V, the Pitzer–Debye–Hückel slope was either calculated or taken from the method and compilations of Bradley and Pitzer (*8*), Rogers and Pitzer (*4*) and Ananthaswamy and Atkinson (*9*). α and b are 2.0 and 1.2 $(\text{kg/mol})^{1/2}$8 respectively, while R is 83.1441 $\text{cm}^3\ \text{bar mol}^{-1}\ \text{K}^{-1}$.

A nonlinear least-squares program was employed for generating Pitzer's coefficients by using eq 3, 4, and 5. Rogers and Pitzer (*4*) reported that the $(\partial\beta^{(1)}/\partial P)_T$ term is insignificant at higher molalities and found it difficult to evaluate it for aqueous NaCl solutions. We too find this term to be negligible in aqueous $SrCl_2$. The lower concentration data of Ellis (*2*) were also included in the overall fit. $\phi_V{}^0$ values obtained by Ellis (*2*) were used in eq 3. $(\partial\beta^{(0)}/\partial P)_T$ and $(\partial C^\phi/\partial P)_T$ thus obtained were fitted with the polynomial of the form

$$Y = q_0 + q_1T + q_2T^2 + q_3T^3 \tag{6}$$

Temperature-dependent parameters q_0, q_1, q_2, and q_3 for both Pitzer's parameters are given in Table III. The average standard deviation of the fit for ϕ_V, using Pitzer's equations, is 0.09 $\text{cm}^3\ \text{mol}^{-1}$ from 50 to 200 °C and at 20.27 bar pressure.

Acknowledgment

The late C. V. G. Reddy of Goa helped me in the experimentation and with stimulating discussions.

Registry No. $SrCl_2$, 10476-85-4.

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Vapor–Liquid Equilibria for Model Mixtures of Coal-Derived Liquids. 1. Binary Systems with 2-Methylfuran

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Vapor–liquid equilibria were measured for binary systems of 2-methylfuran with cyclohexane, benzene, thiophene, and pyridine in the region 45–65 °C. Deviations from ideal behavior are small, especially for 2-methylfuran/aromatic binaries. In binary solutions with benzene or cyclohexane, 2-methylfuran shows smaller deviations from ideality than those observed for other aromatic heterocycles (pyridine and thiophene). For nearly ideal mixtures, complex models for the excess Gibbs energy (such as UNIQUAC) may give spurious results. For nearly ideal systems, it is advantageous to use a simple model.

Introduction

Interest in coal liquefaction and gasification tends to be inversely proportional to the availability of petroleum. At various times in this century, there has been significant interest in the use of coal to produce liquid fuels and feedstocks for petrochemicals (*1*). Such interest has been sporadic, always coinciding with periods of high relative petroleum cost.

To design efficient separation operations, it is necessary to appreciate the differences between petroleum-derived and coal-derived liquids. For engineering design, a primary concern is to understand vapor–liquid equilibria of coal-derived liquids.

The chemical composition of coal (*2*) differs significantly from that of oil. A major distinction is the heteroatom content. The sulfur, nitrogen, and oxygen content of coal (*3*) is typically an order of magnitude above that in oil (independent of whatever inorganic material may be present in the coal). To predict phase equilibria for mixtures containing coal-liquefaction products, it is necessary to know the influence of the heteroatom groups on fluid-phase thermodynamic properties.

The oxygen content of bituminous coal is usually about 15 wt % on a moisture and ash-free basis (*1*). The predominant functional groups include phenols, ethers, carboxylic acids, carbonyls, and furans. We are particularly interested in furans because deoxygenation of heterocyclic oxygen is more difficult than that for oxygen outside of a ring structure (*4*).

There is a paucity of vapor–liquid equilibrium data for mixtures containing aromatic, oxygen heterocycles. We are not aware of any vapor–liquid equilibrium data in the literature for mixtures of furan or a substituted furan with benzene (or any other aromatic) or with any alkane other than butane (*5*). Such data are necessary to provide a data base for estimation methods such as UNIFAC (*6*) or ASOG (*7*).

In part 1 of this work, we report vapor–liquid equilibria for binary mixtures of 2-methylfuran with benzene, cyclohexane, thiophene, and pyridine. Part 2 presents results for binary mixtures containing bicyclic and high-boiling compounds (diphenyl ether, tetralin, *m*-cresol, 1-methylnaphthalene, quinoline, aniline, and benzothiazole). Part 3 reports vapor–liquid equilibrium data for ternary systems containing one aromatic heterocycle (2-methylfuran, thiophene, pyridine, or pyrrole) with benzene and cyclohexane.

Experimental Section

All chemicals are commercially available. Benzene, cyclohexane, pyridine, and thiophene were spectrophotometric or high-purity grade; they were not purified further. The 2-

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

press., kPa	x_1	y_1	press., kPa	x_1	y_1
	45.7 °C			65.8 °C	
30.85	0.00	0.00	63.17	0.00	0.00
32.92^a	0.0325	0.0883	66.00	0.0249	0.0643
33.80	0.0519	0.1309	66.65	0.0352	0.0835
37.68	0.1302	0.2812	76.82	0.1445	0.2859
39.92	0.1840	0.3489	78.09	0.1638	0.3091
43.07	0.2773	0.4568	84.90	0.2599	0.4277
45.20	0.3472	0.5197	89.76^b	0.3518	0.5141
45.99	0.3785	0.5406	90.74	0.3669	0.5268
48.10	0.4753	0.6111	95.32	0.4679	0.6062
49.54	0.5573	0.6665	98.67	0.5501	0.6646
51.38	0.6808	0.7487	102.63	0.6793	0.7502
52.24	0.7614	0.8023	104.39	0.7588	0.8043
52.80	0.8276	0.8500	105.68	0.8253	0.8517
53.28	0.8789	0.8895	106.37^b	0.8752	0.8924
53.48	0.9506	0.9513	107.82	0.9494	0.9528
53.58	1.00	1.00	107.89	1.00	1.00

^{a} 45.8 °C. ^{b} 65.7 °C.

methylfuran was reagent grade and was purified by distillation under vacuum with a 15-tray Oldershaw column. The purity of all chemicals, as measured by gas chromatography, was greater than 99.9%.

Vapor-liquid equilibria were measured by a "Labodest" Phasengleichgewichts Apparatur (0601/U) manufactured by the Fischer Gesellschaft (Meckenheim, Federal Republic of Germany). This is a recirculating still of the type described by Walas (*8*). The temperature was measured with a Fischer digital thermometer and the pressure with a Pennwalt/Wallace and Tiernan (Belleville, NJ) FA-107 Absolute Calibration Standard. The thermometer was calibrated against the vapor pressure of pure cyclohexane as measured by the National Bureau of Standards (*9*). Pure-component vapor pressures were also measured with the recirculating still.

Vapor and liquid compositions were measured by gas chromatography (GC). One-microliter samples, withdrawn from the vapor and liquid streams of the still, were analyzed with an Aerograph 1520 GC equipped with a thermal-conductivity detector (Carle Model 100 Micro Detector System). GC responses peaks were integrated by using a Varian Model CDS-111 Chromatography Data System. The GC columns were packed with 15% FFAP/Chromosorb W-HP (3.0-m columns for benzene and cyclohexane; 2.0-m columns for thiophene) or Carbowax 20M/Chromosorb W-HP (2.0-m columns for pyridine) supplied by Waters Associates.

The GC was calibrated with gravimetrically prepared standard solutions. At least two analyses were made of each liquid and each vapor composition.

Safe experimental technique is imperative when working with the chemicals studied. Benzene is carcinogenic; pyridine is significantly toxic. Thiophene and pyridine are foul-smelling. All chemicals were weighed and measured in a fume hood. GC calibration standards were stored in sealed septum bottles. The recirculating still is totally enclosed within a fume box. No fumes were released during composition sampling; samples were withdrawn through septa in the still and closeable windows in the fume box. The GC effluent is purged into a fume hood and excess syringe material is rejected into waste septum bottles. Disposable plastic gloves were used whenever chemicals were transferred.

Results and Discussion

Tables I–IV give experimental data (*P*, *T*, *x*, *y*). Two isotherms were measured for binary systems containing cyclohexane, benzene, and thiophene; one isotherm was measured for the pyridine system. To illustrate the results, Figure 1 shows data for 2-methylfuran/thiophene.

Table II. Vapor–Liquid Equilibria for the System 2-Methylfuran (1)/Thiophene (2)

press., kPa	x_1	y_1	press., kPa	x_1	y_1
	45.7 °C			65.8 °C	
26.43	0.00	0.00	55.85	0.00	0.00
27.25^a	0.0289	0.0596	57.75	0.0321	0.0609
28.63^a	0.0743	0.1441	59.51	0.0670	0.1251
32.02^a	0.1830	0.3219	66.01^b	0.1805	0.3097
33.79	0.2491	0.4105	69.68^b	0.2452	0.3979
35.60	0.3119	0.4864	73.24	0.3095	0.4731
38.17^a	0.4024	0.5814	78.01	0.3994	0.5699
39.45	0.4490	0.6241	80.60	0.4438	0.6115
40.42	0.4906	0.6623	82.55	0.4894	0.6503
42.96	0.5838	0.7325	87.35	0.5764	0.7244
45.22	0.6746	0.7997	91.81	0.6730	0.7949
47.30	0.7552	0.8560	95.83	0.7522	0.8495
49.53	0.8450	0.9106	100.16	0.8419	0.9066
51.77	0.9311	0.9611	104.72	0.9300	0.9594
53.58	1.00	1.00	107.89	1.00	1.00

^{a} 45.8 °C. ^{b} 65.7 °C.

Table III. Vapor–Liquid Equilibria for the System 2-Methylfuran (1)/Benzene (2)

press., kPa	x_1	y_1	press., kPa	x_1	y_1
	50.8 °C			65.8 °C	
37.27	0.00	0.00	63.81	0.00	0.00
37.97	0.0255	0.0442	64.88	0.0245	0.0417
39.64	0.0807	0.1333	68.21	0.0969	0.1550
41.52	0.1452	0.2300	71.46	0.1676	0.2569
42.00^a	0.1698	0.2627	72.14^b	0.1821	0.2765
47.20	0.3533	0.4835	78.25	0.3163	0.4409
49.74	0.4418	0.5755	84.00	0.4404	0.5712
52.16	0.5322	0.6582	87.93	0.5311	0.6547
57.56	0.7343	0.8194	96.62	0.7332	0.8181
59.50	0.8119	0.8762	99.97	0.8101	0.8740
60.90^a	0.8746	0.9189	102.27^b	0.8730	0.9170
62.59^a	0.9342	0.9584	105.85^c	0.9348	0.9580
64.31	1.00	1.00	107.89	1.00	1.00

^{a} 50.7 °C. ^{b} 65.7 °C. ^{c} 65.9 °C.

Table IV. Vapor–Liquid Equilibria for the System 2-Methylfuran (1)/Pyridine (2) at 65.8 °C

press., kPa	x_1	y_1	press., kPa	x_1	y_1
18.77	0.00	0.00	75.99	0.6132	0.8959
20.59	0.0165	0.1022	84.20	0.7142	0.9294
22.97	0.0383	0.2099	88.03	0.7610	0.9434
24.84	0.0561	0.2836	93.39^a	0.8231	0.9589
44.76^a	0.2525	0.6770	100.76^a	0.9120	0.9812
55.52	0.3719	0.7803	102.12	0.9283	0.9843
64.21^a	0.4687	0.8367	107.89	1.00	1.00

^{a} 65.9 °C.

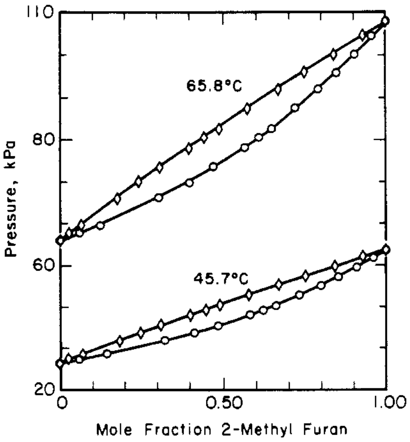

Figure 1. Vapor-liquid equilibria for the system 2-methylfuran/thiophene.

Table V. Vapor Pressure of Pure 2-Methylfuran

temp, °C	press., kPa	temp, °C	press., kPa
35.7	36.23	55.8	77.12
40.7	44.28	60.8	91.43
45.7	53.58	65.8	107.89
50.8	64.31		

The gas-chromatograph calibration data are given in the supplementary material (Table S-I). Table V gives the saturated vapor pressure of pure 2-methylfuran as a function of temperature.

For every component i, the equation of equilibrium is

$$\phi_i y_i P = x_i \gamma_i \phi_i^{\text{sat}} P_i^{\text{sat}} \exp\left[\frac{v_i(P - P_i^{\text{sat}})}{RT}\right] \qquad (1)$$

where ϕ is fugacity coefficient, y vapor-phase mole fraction, P total pressure, γ activity coefficient at system T and P, x liquid-phase mole fraction, T temperature, ϕ^{sat} pure-component fugacity coefficient at saturation, P^{sat} pure-component saturation pressure, v liquid molar volume, and R universal gas constant.

The exponential term (Poynting correction) is very nearly unity for the experimental conditions of this study.

Liquid molar volumes were taken from the data compilation reported by Reid et al. (*10*) or, if unavailable, estimated by the method of Hankinson and Thomson (*11*).

The data were regressed by a maximum-likelihood procedure (*12*, *13*) to determine binary parameters for the Van Laar, NRTL, and UNIQUAC models for the excess Gibbs energy, which is directly related to the activity coefficients (*14*). These binary parameters are given in Table VI, and the equations used for correlation are summarized in Table VII. The regression procedure weighs each individual measurement according to the experimental uncertainty. Table S-II (supplementary material) gives standard deviations for each measurement of the pressure, temperature, and vapor and liquid compositions.

The largest sources of experimental uncertainty come from temperature and composition measurements. The temperature could only be measured to one-tenth of a degree Celsius. With no other errors, this uncertainty implies that the saturated vapor pressure of pure 2-methylfuran at 65.8 °C could range from 107.68 to 108.03 kPa.

A single analysis of the vapor or liquid composition by gas chromatography is frequently imprecise. However, with multiple measurements, the standard deviation of a composition analysis was usually less than 0.0010 mole fraction.

Vapor-phase nonidealities are small; they were calculated by the method of Hayden and O'Connell (*15*) as discussed by Prausnitz et al. (*13*). All of the vapor-phase fugacity coefficients estimated by the Hayden–O'Connell method for this study were between 1.00 (ideal) and 0.95. In addition, data reduction was also performed neglecting vapor-phase corrections. Binary parameters for models of the excess Gibbs energy, assuming ideal vapor-phase behavior, are given in the supplementary material (Table S-III).

Table VI lists the mean deviations between experimental and calculated pressures, temperatures, and compositions for each isotherm. In each case, these deviations are less than the estimated experimental uncertainty. The data are thermodynamically consistent according to the criteria of Van Ness et al. (*16*) and Christensen and Fredenslund (*17*).

All of the systems show positive deviations from Raoult's law. However, only the 2-methylfuran/cyclohexane system shows significant deviations. Figure 2 shows calculated activity coefficients for the isotherm at 65.8 °C. The 2-methylfuran/aromatic systems show very small deviations from ideality. For the pyridine isotherm, all calculated activity coefficients are between 1.00 and 1.20; for the thiophene isotherms, between 1.00 and 1.10; for benzene, between 1.00 and 1.05. Indeed, for the 2-methylfuran/benzene system, all deviations from both liquid and vapor ideality are within experimental uncertainty.

The qualitative results may be easily summarized. The aromatic 2-methylfuran has a higher activity coefficient in alkanes than in aromatics. The activity coefficient of 2-methylfuran in

Table VI. Binary Parameters for the UNIQUAC, Van Laar, and NRTL Models for the Excess Gibbs Energy:[a] Binary Systems with 2-Methylfuran

				root-mean-squared dev			
temp, °C	model	$P(1)$[b]	$P(2)$[b]	P, kPa	T, °C	x	y
			Cyclohexane				
45.7	UNIQUAC	13.76	47.91	0.01	0.1	0.0013	0.0014
	NRTL	130.7	244.7	0.01	0.1	0.0013	0.0014
	Van Laar	0.579	0.549	0.01	0.1	0.0013	0.0014
65.8	UNIQUAC	59.57	−2.96	0.01	0.0	0.0009	0.0004
	NRTL	274.0	66.60	0.01	0.0	0.0009	0.0004
	Van Laar	0.459	0.502	0.01	0.0	0.0009	0.0004
			Thiophene				
45.7	UNIQUAC	98.04	−74.90	0.02	0.1	0.0009	0.0011
	NRTL	218.8	−150.4	0.02	0.1	0.0009	0.0011
	Van Laar	0.075	0.090	0.02	0.1	0.0009	0.0011
65.8	UNIQUAC	212.0	−150.9	0.02	0.1	0.0009	0.0017
	NRTL	684.7	−474.2	0.02	0.1	0.0009	0.0017
	Van Laar	0.059	0.158	0.02	0.1	0.0010	0.0018
			Benzene				
50.8	UNIQUAC	10.21	−3.08	0.01	0.0	0.0006	0.0007
	NRTL	−170.3	209.6	0.01	0.0	0.0006	0.0007
	Van Laar	0.040	0.031	0.01	0.0	0.0006	0.0007
65.8	UNIQUAC	158.9	−122.8	0.01	0.0	0.0005	0.0004
	NRTL	534.1	−411.5	0.01	0.0	0.0005	0.0004
	Van Laar	0.022	0.071	0.01	0.1	0.0005	0.0005
			Pyridine				
65.8	UNIQUAC	195.1	−126.5	0.02	0.1	0.0009	0.0014
	NRTL	438.1	−243.2	0.02	0.1	0.0009	0.0014
	Van Laar	0.176	0.250	0.02	0.1	0.0009	0.0014

[a] Vapor-phase nonidealities calculated by use of the Hayden–O'Connell method. [b] The dimensions of parameters $P(1)$ and $P(2)$ for the UNIQUAC and NRTL models are calories/mole; they are dimensionless for the Van Laar model.

Table VII. Models for the Excess Gibbs Energy[a]

g^E = molar excess Gibbs energy
R = universal gas constant
T = temperature (absolute)

UNIQUAC Equation

$$\frac{g^E}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + 5\left(q_1x_1 \ln \frac{\theta_1}{\Phi_1} + q_2x_2 \ln \frac{\theta_2}{\Phi_2} \right) - q_1x_1 \ln (\theta_1 + \theta_2\tau_{21}) - q_2x_2 \ln (\theta_2 + \theta_1\tau_{12})$$

where

$$\tau_{ij} = \left(\frac{-\Delta u_{ij}}{RT} \right)$$

$$\theta_i = \frac{x_iq_i}{x_iq_i + x_jq_j};\ \Phi_i = \frac{x_ir_i}{x_ir_i + x_jr_j}$$

r = UNIQUAC volume parameter
q = UNIQUAC area parameter

$P(1) = \Delta u_{12}$; $P(2) = \Delta u_{21}$

NRTL Equation

$$\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}} \right)$$

where

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT};\ G_{ij} = \exp(-0.30\tau_{ij})$$

$P(1) = \Delta g_{12}$; $P(2) = \Delta g_{21}$

Van Laar Equation

$$\frac{g^E}{RT} = \frac{A_{12}A_{21}x_1x_2}{A_{12}x_1 + A_{21}x_2}$$

$P(1) = A_{12}$; $P(2) = A_{21}$

[a] The dimensions of parameters $P(1)$ and $P(2)$ in the UNIQUAC and NRTL equations are calories per mole; for the Van Laar equation, $P(1)$ and $P(2)$ are dimensionless.

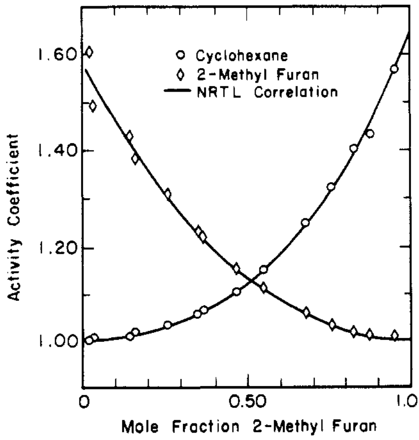

Figure 2. Activity coefficients for the system 2-methylfuran/cyclohexane at 65.8 °C.

solution with another aromatic appears to increase slightly with increasing polarity of the other component.

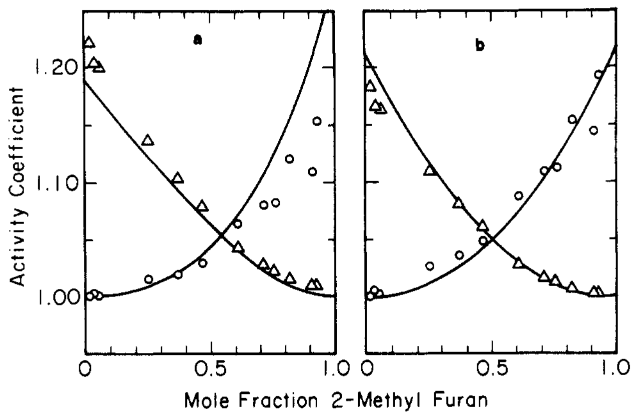

Figure 3. (a) Activity coefficients for the system 2-methylfuran/pyridine at 66 °C. Vapor-phase nonideality calculated by the method of Hayden and O'Connell (*15*). (b) Activity coefficients for the system 2-methylfuran/pyridine at 66 °C. Ideal vapor phase assumed.

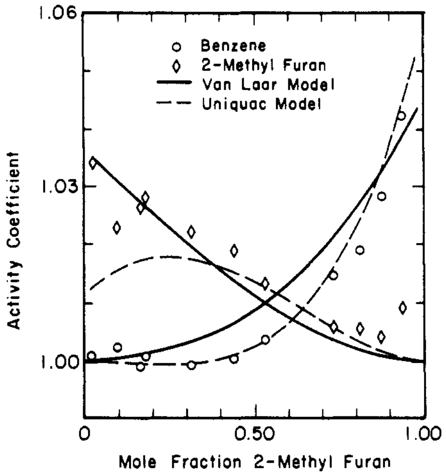

Figure 4. Activity coefficients for the system 2-methylfuran/benzene at 65.8 °C.

In binary solutions with benzene or cyclohexane, 2-methylfuran shows smaller deviatiбns fromn ideality than do either pyridine (*18*, *19*) or thiophene (*20*, *21*). Such heterocyclic structures (containing oxygen, nitrogen, or sulfur) are usually present in coal.

The Hayden–O'Connell method provides a technique for estimating vapor-phase fugacity coefficients. However, these estimates may be subject to considerable uncertainty whenever, as here, binary vapor-phase parameters are not known accurately. Such uncertainty is usually of minor consequence, but may be a cause of error when the Hayden–O'Connell method is used to estimate fugacity coeffcients for a system where the vapor-phase and liquid-phase behavior are both nearly ideal. Figure 3 shows activity coefficients for the 2-methylfuran/pyridine system. This figure suggests that the activity coefficients and their correlation are improved by considering the vapor phase to be ideal (Figure 3b) rather than nonideal as estimated by the Hayden–O'Connell method (Figure 3a). Similar behavior was found for the 2-methylfuran/thiophene isotherm at 65.8 °C (but not at 45.7 °C). For nearly ideal systems at low pressures, such as these, complicated models for vapor-phase nonideality (such as the Hayden–O'Connell model) appear to offer little benefit.

Similar spurious results can occur when modeling liquid-phase behavior of nearly ideal systems. Models for the excess Gibbs energy, such as UNIQUAC, are needlessly complex for such well-behaved systems. For systems with small deviations from ideality (such as 2-methylfuran/benzene), a complex model tends to correlate experimental error, as illustrated in Figure 4, which uses a highly expanded scale.

In Figure 4, two of the calculated activity coefficients for benzene are below unity (the lowest is 0.9991). The UNIQUAC 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.

Acknowledgment

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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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