$$\Lambda_{21} = \frac{V_{1,L}}{V_{2,L}} \exp\left(\frac{-\lambda_{21} - \lambda_{22}}{RT}\right) \qquad (10)$$

Here $V_{1,L}$ and $V_{2,L}$ are the liquid molar volumes and $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ are the model parameters with $\lambda_{12} = \lambda_{21}$. The Wilson parameters, obtained by minimizing the objective function defined by eq 1, are reported in Table V. All the three sets of data at 300, 500, and 700 mmHg were used in data reduction.

The excess Gibbs energies at 25 °C for the three systems were also calculated with these model parameters by using the equation

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (11)$$

and are presented in Table VI.

Glossary

A, B, C	Antoine constants
p	pressure, mmHg
t	temperature, °C
x	mole fraction in liquid phase
y	vapor composition

Greek Letters

γ	activity coefficient
Λ	Wilson parameter

Subscripts

1	methyl ethyl ketone
2	substituted benzene

Registry No. MEK, 78-93-3; *o*-dichlorobenzene, 95-50-1; bromobenzene, 108-86-1; nitrobenzene, 98-95-3.

Literature Cited

(1) Riddick, J. A.; Bunger, W. B. *Organic Solvents*, 3rd ed.; Wiley Interscience: New York, 1970.
(2) Timmermans, J. *Physico-chemical Properties of Pure Organic Compounds*; Elsevier: Amsterdam, 1950.
(3) Spencer, C. F.; Danner, R. P. *J. Chem. Eng. Data* **1972**, *17*, 236.
(4) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(5) Boublik, T.; Fried, V.; Hala, E. *The Vapour Pressures of Pure Substances*; Elsevier: Amsterdam, 1973.
(6) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1977.
(7) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.

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Vapor–Liquid Equilibria for *m*-Cresol/Tetralin and Tetralin/Quinoline at Temperatures between 523 and 598 K

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Binary vapor–liquid equilibria are reported for the binary systems of *m*-cresol/tetralin and tetralin/quinoline at 523.15, 548.15, 573.15, and 598.15 K as well as tetralin vapor pressures over the same temperature region. These compounds are of interest because they form highly nonideal mixtures and are also models for coal liquids. Due to hydrogen-bonding capabilities, both *m*-cresol and quinoline are quite hygroscopic. Water was found to be a major impurity and had very large effects on the vapor–liquid equilibria measurements, even at extremely low concentrations. The *m*-cresol/tetralin data indicated a low-boiling azeotrope that moved toward higher *m*-cresol concentrations and eventually disappeared as the temperature increased. The tetralin/quinoline system exhibited small departures from ideal behavior.

Introduction

As part of a continuing effort (*1*, *2*) to study the phase behavior of coal-derived liquid model compounds, vapor–liquid equilibria (VLE) measurements were generated for the binary systems *m*-cresol/1,2,3,4-tetrahydronaphthalene (tetralin) and tetralin/quinoline at the four isotherms 523.15, 548.15, 573.15, and 598.15 K as well as vapor pressure data for tetralin. Phase behavior data are important not only for use in engineering design and analysis, but also to check thermodynamic property correlations. Only a limited amount of phase behavior data is available for highly nonideal systems and even less data exist at elevated conditions where many chemical processes operate.

Previously reported work (*2*) studied the binary system of *m*-cresol/quinoline to model the interactions between an acidic oxygen compound and a basic nitrogen compound which are likely to be found in coal liquids. Both binary vapor–liquid equilibrium (VIE) data at 523.15, 548.15, 573.15, and 598.15 K and vapor pressure data over the same temperature range for pure *m*-cresol and quinoline were reported. The present study considers the interactions between an acidic oxygen compound (*m*-cresol) and a naphthenic compound (tetralin) as well as the interactions between a basic nitrogen compound (quinoline) and a naphthenic compound (tetralin). Complementary enthalpy data for the *m*-cresol/quinoline, *m*-cresol/tetralin, and tetralin/quinoline systems have been obtained at the Colorado School of Mines (*3*, *4*) over a temperature range of 291–650 K and pressures of 101.3–10342 kPa.

A major problem in obtaining the VLE data was that both *m*-cresol and quinoline are capable of hydrogen bonding and consequently are hygroscopic. Trace amounts of water can significantly affect the measured vapor pressure especially for systems containing *m*-cresol. Estimations of the effects of water on our measurements have been previously reported (*2*).

Experimental Details

The experimental apparatus for obtaining these measurements has been discussed in detail previously (*1*). The measurements were made on a flow vapor–liquid equilibrium apparatus and analyzed on a Hewlett-Packard 5710A gas chromatograph with a flame ionization detector. The flow system is advantageous for compounds that decompose at high temperatures since the residence time in the heated portion of the flow system is only about 5 min. Estimated experimental error

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Table I. Tetralin Vapor Pressures

temp, K	press., kPa	temp, K	press., kPa
506.6	175.8	573.1	583.4
514.8	207.5	578.4	632.0
528.7	274.8	587.9	731.0
539.0	331.3	595.3	809.2
553.2	420.9	603.5	908.5
556.2	445.4	613.3	1029.9

in the temperature measurements is ±0.1 K. Experimental error in the pressure measurements was estimated as ±0.7 kPa below 689.5 kPa and ±3.5 kPa between 689.5 and 3500 kPa. The accuracy of the GC analyses was shown to be ±0.001 mole fraction. This accuracy was determined by analyzing samples whose concentrations were known by weight.

The *m*-cresol was purchased from Sigma Chemical Co. with a stated purity of 99%. By gas chromatographic analysis, the purity was typically found to be 99.8% on a water-free basis. The water content was difficult to determine below 0.1% water by a Karl Fischer titration. All of the *m*-cresol was distilled in a Perkin Elmer spinning band distillation column to remove the water. Vapor pressure measurements corresponded well with literature data, indicating successful removal of contaminants.

Synthetic quinoline was purchased from J. T. Baker and Alfa Products at a purity level of 99%. Synthetic quinoline was required since other sources of quinoline had significant quantities of isoquinoline as a contaminant. The quinoline was distilled to raise the purity to 99.9%, as determined by gas chromatography, and to eliminate water.

Tetralin was purchased from Aldrich Chemical Co. at a purity of 99%. The tetralin had a low-boiling contaminant that was difficult to remove and required slow takeoff rates on the distillation column. Again, the final product was shown to be 99.9%+ pure by gas chromatography analysis. An added difficulty was that tetralin decomposes significantly even at room temperatures. At the temperatures of this study, the rate of decomposition is rapid.

Samples were initially purified to 99.9% and the integrity of the samples was monitored while the physical measurements were being made. If decomposition products increased to a level above 0.1 area %, the sample was removed from the system. To prevent reabsorption of water, the experimental apparatus was isolated from the atmosphere. However, if the pressure measurements appeared to be inconsistent, the sample was removed and redistilled.

Experimental Results

Vapor Pressure Measurements. Vapor pressure measurements were generated for tetralin over the temperature range of 523.15–598.15 K. These measurements are presented in Table I. In Figure 1, the data from this research are compared with published data (*8*–*13*) and vapor pressure data generated at the Colorado School of Mines on a flow calorimeter (*4*). Vapor pressure measurements for both quinoline and *m*-cresol have been previously reported (*2*). An acentric factor was calculated for tetralin at T_r = 0.7 and was found to be 0.327 which is significantly different that the previously reported value of 0.303 (*5*) but corresponds very well to a more recently reported value of 0.3278 (*17*). As is also shown in Figure 1, the Soave–Redlich–Kwong equation (*6*) predicts the vapor pressure of tetralin much better if the new acentric factor of 0.327 is used. Previously, little vapor pressure data was available near T_r = 0.7 and it is suspected that the acentric factor was estimated to be similar to that of naphthalene which also has an acentric factor of 0.303 (*5*).

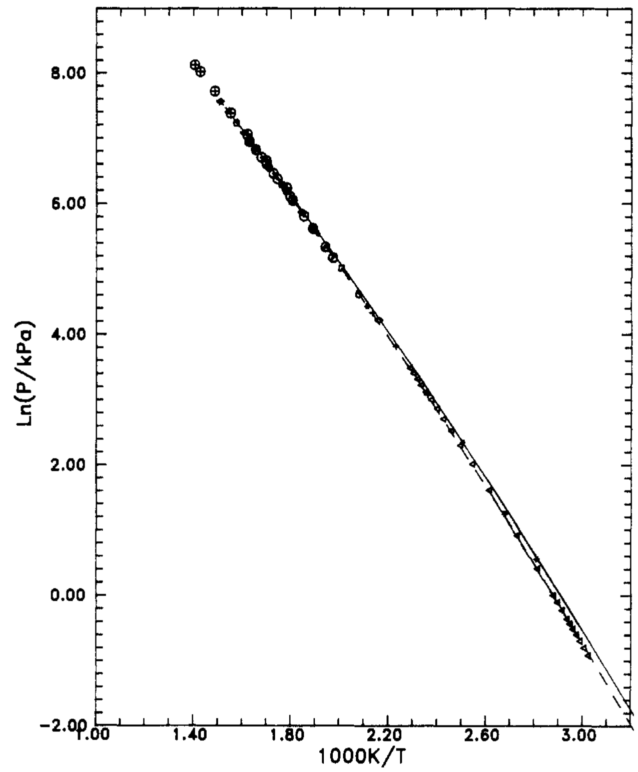

Figure 1. Tetralin vapor pressures: O, Flanigan (*4*); □, Natarajan (*8*); Δ, Katayama (*10*); ◇, Simnick (*11*); +, Krevor (*7*); ×, Kara (*9*); ☆, Nasir (*12*); ⊙, this work; ⊗, Wilson (*13*); —, ω = 0.303; - - -, ω = 0.327.

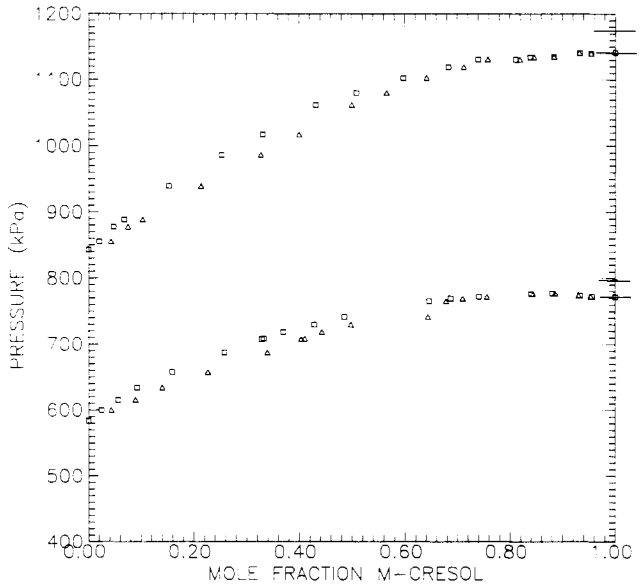

Figure 2. m-Cresol/tetralin VLE data at 573.15 and 598.15: □, liquid and Δ, vapor.

Vapor–Liquid Equilibria Measurements. Listed in Tables II and III and shown in Figure 2 (for only two isotherms) are the VLE data for the *m*-cresol/tetralin system at four isotherms, 523.15, 548.15, 573.15, and 598.15 K. At the lowest isotherms a low-boiling azeotrope is present at high *m*-cresol concentrations. Literature data (*7*) also indicate the presence of an azeotrope at temperatures between 423.15 and 468.15 K that occurs at increasingly higher concentrations of *m*-cresol as the temperature increases. *m*-Cresol is a polar compound capable of hydrogen bonding through the hydroxyl group. *m*-Cresol molecules exhibit a significant degree of association with other *m*-cresol molecules and are quite hygroscopic due to hydrogen bonding with water. Tetralin is relatively nonpolar. In addition, none of the hydrogens on the tetralin molecule are acidic enough to allow hydrogen bonding, to any large extent, with

Table II. VLE Measurements for *m*-Cresol/Tetralin

temp, K	press., kPa	mol % *m*-cresol x	y	$\gamma_1{}^a$	$\gamma_2{}^a$	G^E/RT
523.15	246.0	0.0	0.0			
	254.1	2.2	4.0	1.519	1.011	0.020
	261.9	5.0	8.5	1.461	1.020	0.038
	265.1	6.1	10.2	1.453	1.024	0.045
	270.8	8.7	13.8	1.406	1.031	0.057
	285.0	17.6	25.0	1.321	1.041	0.082
	289.0	20.5	28.5	1.310	1.042	0.088
	300.8	30.7	38.1	1.213	1.073	0.108
	306.8	42.5	49.3	1.154	1.078	0.104
	313.7	55.4	59.3	1.088	1.138	0.104
	315.3	60.6	63.2	1.065	1.170	0.100
	318.8	67.0	68.5	1.054	1.210	0.098
	318.8	72.5	72.9	1.037	1.247	0.087
	318.4	77.9	77.5	1.025	1.287	0.075
	317.4	81.7	80.7	1.015	1.329	0.064
	316.4	84.5	83.4	1.011	1.346	0.055
	314.7	88.9	87.5	1.003	1.408	0.041
	312.6	91.8	90.8	1.002	1.395	0.029
	311.4	95.8	95.0	1.001	1.475	0.017
	308.3	99.4	99.0	0.996	2.046	0.000
	308.3	100.0	100.0			
548.15	386.6	0.0	0.0			
	398.2	2.2	3.8	1.407	1.010	0.017
	410.5	5.0	8.3	1.390	1.018	0.033
	414.4	6.1	10.0	1.385	1.019	0.037
	428.5	10.4	15.7	1.314	1.030	0.055
	439.2	15.9	23.3	1.305	1.020	0.059
	460.6	26.3	34.4	1.215	1.037	0.078
	462.7	28.8	36.7	1.189	1.040	0.078
	474.0	34.9	42.1	1.150	1.062	0.088
	497.3	54.5	59.2	1.081	1.116	0.092
	505.5	62.2	65.4	1.061	1.155	0.091
	506.2	67.8	69.8	1.040	1.185	0.081
	506.9	72.6	73.9	1.030	1.205	0.072
	508.2	75.6	76.4	1.025	1.226	0.068
	509.2	84.3	84.0	1.012	1.294	0.051
	507.0	88.4	87.9	1.006	1.320	0.038
	505.3	92.7	91.9	1.000	1.400	0.025
	505.1	95.6	95.1	1.003	1.404	0.018
	500.3	100.0	100.0			

[a] Activity coefficients referenced to the saturation pressure of *m*-cresol.

Table III. VLE Measurements for *m*-Cresol/Tetralin

temp, K	press., kPa	mol % *m*-cresol x	y	$\gamma_1{}^a$	$\gamma_2{}^a$	G^E/RT
573.15	583.4	0.0	0.0			
	599.5	2.5	4.3	1.385	1.004	0.012
	615.1	5.6	8.9	1.309	1.009	0.023
	633.6	9.2	14.0	1.286	1.015	0.036
	657.3	15.9	22.7	1.246	1.015	0.047
	687.1	25.8	33.9	1.191	1.020	0.060
	707.5	32.9	40.4	1.141	1.041	0.070
	708.0	33.3	41.1	1.147	1.035	0.069
	718.1	37.0	44.3	1.127	1.049	0.074
	729.5	42.9	49.8	1.107	1.056	0.075
	741.2	48.6	54.4	1.082	1.079	0.078
	765.1	64.6	67.8	1.042	1.134	0.071
	769.5	68.7	71.0	1.031	1.161	0.068
	772.1	74.1	75.6	1.021	1.184	0.059
	775.7	84.1	84.4	1.008	1.237	0.041
	777.0	88.1	88.6	1.012	1.210	0.033
	773.9	93.3	93.0	0.999	1.315	0.018
	772.3	95.6	95.3	0.997	1.342	0.011
	771.5	100.0	100.0			
598.15	842.8	0.0	0.0			
	855.0	2.1	4.3	1.620	0.989	–0.001
	877.2	4.8	7.5	1.263	1.003	0.014
	888.2	6.8	10.3	1.237	1.003	0.017
	939.0	15.3	21.4	1.197	1.009	0.035
	986.0	25.3	32.7	1.151	1.016	0.048
	1017.0	33.1	40.0	1.103	1.035	0.056
	1061.7	43.2	50.0	1.094	1.048	0.066
	1079.9	50.9	56.6	1.065	1.066	0.063
	1102.6	59.7	64.1	1.045	1.090	0.061
	1119.0	68.3	71.2	1.027	1.124	0.055
	1130.6	74.0	75.8	1.017	1.160	0.051
	1130.4	81.1	81.9	1.003	1.193	0.035
	1133.9	83.9	84.6	1.003	1.195	0.031
	1134.2	88.4	88.4	0.995	1.249	0.022
	1140.0	93.3	93.2	0.998	1.273	0.015
	1139.3	95.4	95.4	0.999	1.253	0.009
	1141.1	100.0	100.0			

[a] Activity coefficients referenced to the saturation pressure of *m*-cresol.

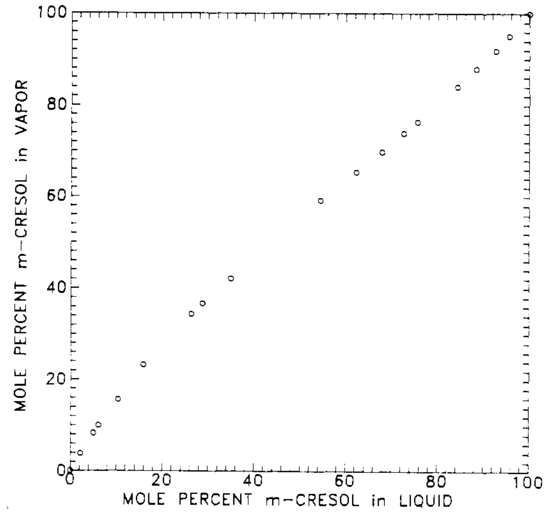

Figure 3. *XY* plot for *m*-cresol/tetralin at 548.15 K.

either *m*-cresol or quinoline. For the *m*-cresol/tetralin binary, the hydrogen bonding between the *m*-cresol molecules is disrupted by the nonpolar tetralin molecules resulting in a low-boiling azeotrope. As illustrated in Figure 2, the azeotrope moves toward higher *m*-cresol concentrations and eventually disappears as the temperature increases.

A small degree of scatter is present in the *Pxy* plot of the VLE data. In Figure 3, typical *x*–*y* data are plotted for the 548.15 K isotherm. It can be seen that a smooth curve is formed by the *x*–*y* data. Since the VLE apparatus used was a flow system operating at different flow rates, the smooth curve indicates that equilibrium was attained. Therefore, it appears that the system was at equilibrium and scatter in the *Pxy* plot is either due to errors in the temperature or pressure measurements. Because of the water contamination problem and difficulties in obtaining experimentally reproducible pressures, it is believed that the scatter results from errors in the vapor pressure due to trace amounts of water. Figure 2 has two marks at 100% *m*-cresol for each isotherm. The distance between the two marks is the error that would result if a 0.01% water contamination was present (*2*). It is obvious that the error due to water concentrations well below 0.01% would still be quite significant. While the samples were purified, traces of water could have been reabsorbed from the atmosphere due to the hygroscopic nature of these compounds.

Activity coefficients were calculated from the binary VLE data. Due to the data being at elevated pressures, it could no longer be assumed that the vapor phase was ideal and that there was no effect of pressure on the liquid-phase activity coefficient. Corrections were made in the calculation of the activity coefficients to account for these nonidealities as discussed by Niesen et al. (*1*) and as shown in the equation

$$\gamma_i = (y_i P / x_i P_{i,\mathrm{sat}})(\hat{\phi}_i{}^{\mathrm{V}} / \phi_{i,\mathrm{sat}})((\hat{f}_i{}^{\mathrm{L}*} / \hat{f}_i{}^{\mathrm{L}*} / \hat{f}_i{}^{\mathrm{L,P}}) / (f_i{}^{*} / f_{i,\mathrm{sat}})) \quad (1)$$

where γ_i is activity coefficient, y_i and x_i are the vapor and liquid

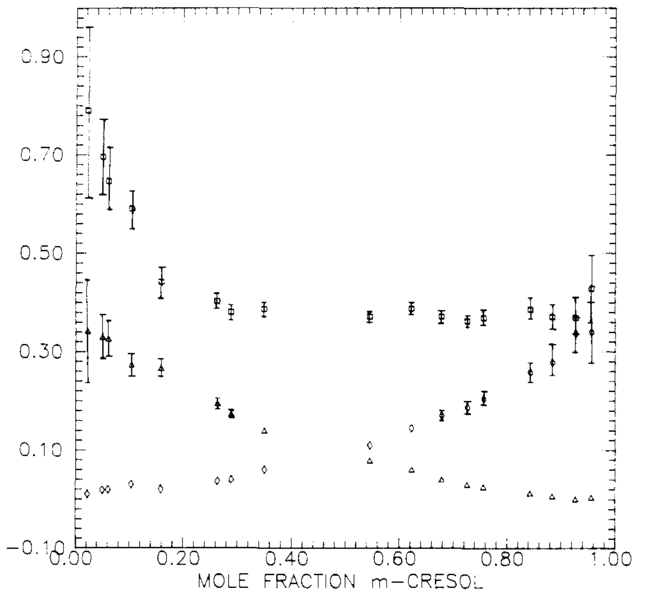

Figure 4. Activity coefficients and excess Gibbs free energies for the *m*-cresol/tetralin system at 548.15 K: △, ln γ_1; ◇, ln γ_2; □, G^E/RTx_1x_2.

mole fractions, P is the system pressure, $P_{i,sat}$ is the saturation vapor pressure of pure i, $(\hat{\phi}_i^V/\phi_{i,sat})$ is the vapor-phase correction for nonidealities, $(\hat{f}_i^{L*}/\hat{f}_i^{L,P})$ is the correction of the nonisobaric acitivity coefficients to constant pressure, and $(f_i^*/f_{i,sat})$ is the Poynting correction term. The fugacity coefficients were calculated from the Soave-Redlich-Kwong equation of state (*6*). The excess Gibbs free energy (G^E/RT) was calculated by using eq 2. The activity coefficients as well

$$G^E/RT = \sum x_i \ln \gamma_i \qquad (2)$$

as the excess Gibbs free energy are listed in Tables II and Tables III. The activity coefficients are greater than 1.0 and become closer to 1.0 as the temperature increases, indicating that at higher temperatures the binary system becomes more ideal. Figure 4 presents a plot of ln γ_1, ln γ_2, and G^E/RTx_1x_2 versus x_1 (mole fraction *m*-cresol) for the 548.15 K isotherm. The error bars in Figure 4 represent ±1 standard deviation assuming the previously stated experimental errors of ±0.001 mole fraction for x and y and ±0.7 kPa for pressure. The method used to calculate the standard deviations is described by Van Ness et al. (*14*). Temperature is also subject to random fluctuations, but this shows up as error in other variables.

While the experimental errors are reasonable for this type of work, they propagate into relatively large errors in the thermodynamic properties. The data at the extreme concentrations are greatly affected by errors in x and y, while the errors in the intermediate concentrations are primarily influenced by pressure. The stated experimental error for pressure (±0.7 kPa) is strictly related to the accuracy of the pressure gauge. Other errors in the pressure measurements due to impurities could not be estimated. However, since we know that impurities were possible (water and/or decompositions products), the error in the presence measurements and, consequently, the error in the thermodynamic properties could be substantially greater.

In view of the effects of the experimental errors in the thermodynamic properties, a thermodynamic consistency test was only marginally useful and only qualitative results are reported. A differential consistency test (as described by Van Ness et al. (*15*, *16*)) was attempted. The internal consistency of the data between 0.1 and 0.9 mole fraction *m*-cresol appeared good. However, due to the large effects of the experimental errors at the extreme concentrations, it was impossible to determine the consistency of the data between 0–0.1 and 0.9–1.0 mole fraction *m*-cresol. Likewise, fitting the data to an activity coefficient model proved unprofitable.

Table IV. VLE Measurements for Tetralin/Quinoline

temp, K	press., kPa	mol % tetralin x	mol % tetralin y	γ_1^b	γ_2^b	G^E/RT
523.15	134.6[a]	0.0	0.0			
	140.7	4.1	8.7	1.256	0.998	0.007
	151.0	10.2	18.8	1.167	1.015	0.029
	161.3	18.0	30.4	1.138	1.015	0.035
	182.6	32.6	46.9	1.090	1.060	0.068
	198.6	45.7	59.0	1.059	1.101	0.078
	213.8	58.9	70.4	1.050	1.126	0.077
	223.5	69.1	78.5	1.040	1.134	0.066
	235.6	82.6	87.9	1.023	1.191	0.049
	238.8	88.8	92.4	1.012	1.177	0.029
	246.0	100.0	100.0			
548.15	221.9	0.0	0.0			
	229.6	3.6	7.4	1.278	0.992	0.001
	243.4	9.9	17.7	1.174	0.997	0.013
	264.7	18.7	30.4	1.154	1.011	0.036
	286.0	30.5	44.2	1.104	1.020	0.044
	313.8	44.7	58.0	1.076	1.052	0.061
	337.2	58.3	69.2	1.051	1.093	0.066
	353.4	68.9	77.9	1.044	1.098	0.059
	369.7	81.7	87.2	1.026	1.126	0.043
	379.8	90.5	93.2	1.014	1.181	0.028
	386.6	100.0	100.0			

[a] Interpolated value. [b] Activity coefficients referenced to the saturation pressure of tetralin.

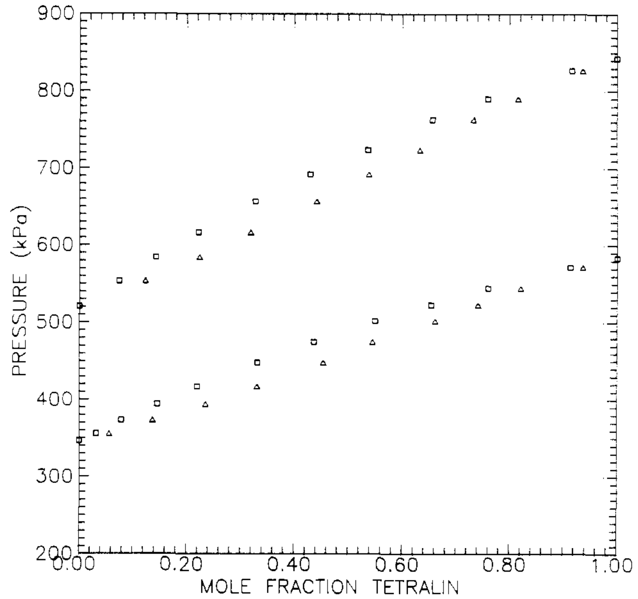

Figure 5. Tetralin/quinoline VLE data at 573.15 and 598.15 K: □, liquid and △, vapor.

Figures 5 and Tables IV and V present the VLE data obtained for the tetralin/quinoline system as well as the calculated activity coefficients and excess Gibbs free energies. Quinoline is polar and capable of hydrogen bonding due to the pair of nonbonded electrons on the nitrogen. However, unlike *m*-cresol, quinoline molecules do not associate to any significant degree with each other since the hydrogens on the molecule are not sufficiently acidic to interact with the nitrogen. Since quinoline molecules do not form strong associations with other quinoline molecules or with tetralin molecules, the tetralin/quinoline binary does not exhibit an azeotrope.

Like *m*-cresol, quinoline is hygroscopic because of the capability to form hydrogen bonds with water. However, as dis-

Table V. VLE Measurements for Tetralin/Quinoline

temp, K	press., kPa	mol % tetralin				
		x	y	γ_1^a	γ_2^a	G^E/RT
573.15	346.2	0.0	0.0			
	355.4	3.2	5.6	1.133	0.999	0.003
	373.1	7.9	13.7	1.173	1.004	0.016
	393.9	14.6	23.6	1.148	1.008	0.027
	416.7	22.0	33.1	1.124	1.017	0.039
	447.9	33.2	45.4	1.089	1.035	0.051
	474.7	43.7	54.6	1.047	1.076	0.061
	501.7	55.1	66.2	1.056	1.056	0.055
	522.6	65.4	74.1	1.031	1.089	0.050
	544.4	76.0	82.1	1.019	1.125	0.042
	571.5	91.3	93.6	1.008	1.158	0.020
	583.4	100.0	100.0			
598.15	520.4	0.0	0.0			
	553.4	7.5	12.3	1.156	1.002	0.013
	584.2	14.3	22.4	1.157	1.004	0.025
	616.3	22.2	31.9	1.111	1.018	0.037
	656.8	32.8	44.2	1.100	1.021	0.045
	691.8	43.0	53.9	1.068	1.041	0.051
	723.5	53.7	63.3	1.043	1.060	0.049
	762.6	65.6	73.3	1.032	1.086	0.049
	789.8	75.9	81.5	1.020	1.106	0.039
	826.6	91.6	93.6	1.006	1.141	0.017
	842.8	100.0	100.0			

[a] Activity coefficients referenced to the saturation pressure of tetralin.

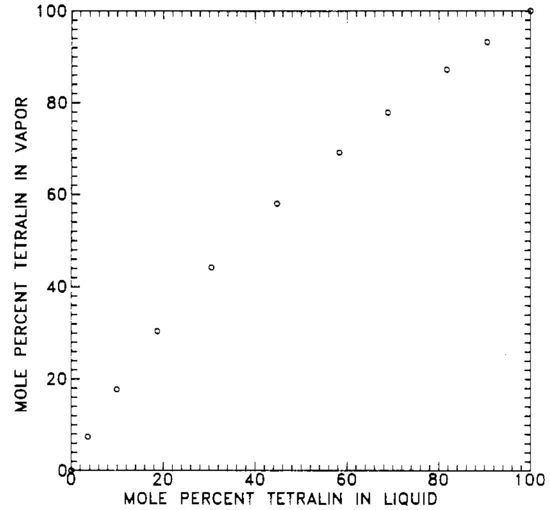

Figure 6. *XY* plot for tetralin/quinoline VLE data at 548.15 K.

cussed previously (*2*), the effects of water contamination are far less substantial for quinoline than for *m*-cresol; consequently, there were fewer experimental problems and the data are much less scattered. Some errors in the pressure measurements may still be present due to the decomposition of tetralin. Figure 6 is an *xy* plot of the 548.15 K isotherm and Figure 7 shows the activity coefficient and excess Gibbs free energies versus the mole fraction of tetralin. The error bars in Figure 7 were calculated as before with the same experimental errors assumed. As would be expected, the activity coefficients are relatively close to 1.0 and the excess Gibbs free energies are small. The results of the consistency test were similar to the *m*-cresol/tetralin system. The data appear to be consistent between 0.1 and 0.9 mole fraction tetralin.

Conclusions

Binary phase behavior data were obtained for the binary systems of *m*-cresol/tetralin and tetralin/quinoline at four isotherms, 523.15, 548.15, 573.15, and 598.15 K. In addition, vapor pressure data for tetralin were reported over the same temperature region and the acentric factor was calculated at $T_r = 0.7$ to be 0.327. The *m*-cresol/tetralin binary exhibits a low-boiling azeotrope that moves toward higher *m*-cresol concentrations with increasing temperature. The tetralin/quinoline binary system does not exhibit large deviations from ideality.

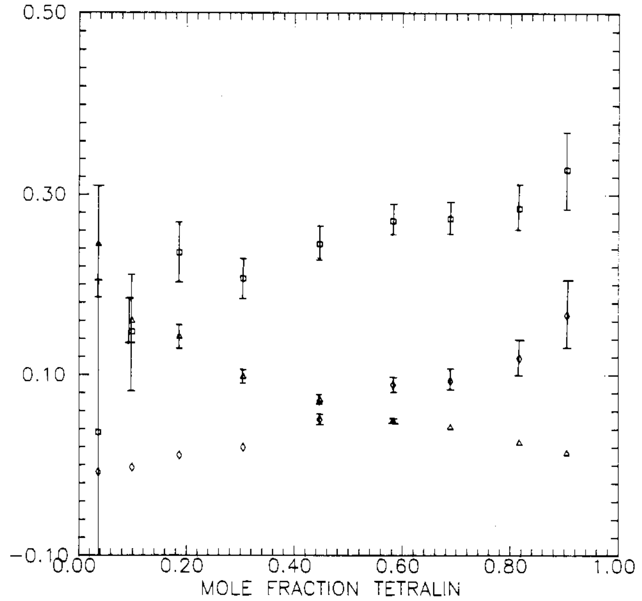

Figure 7. Activity coefficients and excess Gibbs free energies for the tetralin/quinoline system at 548.15 K: △, ln γ_1; ◇, ln γ_2; □, G^E/RTx_1x_2.

Experimental difficulties were encountered due to the extreme hygroscopic nature of the *m*-cresol and quinoline and the decomposition of tetralin. Errors in the pressure measurements due to water contamination were shown to be quite significant for concentrations well below 0.01% water. All samples were purified by distillation and were isolated from the atmosphere to prevent water contamination. Samples were also monitored for contaminants produced from the decomposition of tetralin. The calculated thermodymanic properties were shown to be highly affected by these experimental errors. A qualitative thermodynamic consistency test indicated that data were probably consistent.

Glossary

f	fugacity
G^E	excess Gibbs free energy
P	pressure
R	gas constant
T	temperature
x	liquid-phase mole fraction
y	vapor-phase mole fraction
γ	activity coefficient
ϕ	fugacity coefficient

Registry No. *m*-Cresol, 108-39-4; tetralin, 119-64-2; quinoline, 91-22-5.

Literature Cited

(1) Niesen, V. G.; Palavra, A.; Kidnay, A. J.; Yesavage, V. F. *Fluid Phase Equilib.* **1986**, *31*, 283–298.
(2) Niesen, V. G.; Yesavage, V. F. *J. Chem. Eng. Data*, in press.
(3) Flanigan, D. A. M.S. Thesis 2810, Colorado School of Mines, 1983.
(4) Flanigan, D. A. Ph.D. Thesis 3305, Colorado School of Mines, 1986.
(5) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
(6) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.
(7) Krevor, D. H.; Lam, F. W.; Prausnitz, J. M. *J. Chem. Eng. Data* **1986**, *31*, 353–357.
(8) Natarajan, G.; Viswanath, D. S. *J. Chem. Eng. Data* **1985**, *30*, 137–140.
(9) Kara, M.; Sung, S.; Klinzing, G. E.; Chiang, S. H. *Fuel* **1981**, *60*, 633–634.

(10) Katayama, H.; Harada, Y. *J. Chem. Eng. Data* **1985**, *29*, 373-375.
(11) Simnick, J. J.; Lawson, C. C.; Lin, H. M.; Chao, K. C. *AIChE J.* **1977**, *23*, 469-476.
(12) Nasir, P.; Hwang, S. C.; Kobayashi, R. *J. Chem. Eng. Data* **1980**, *25*, 298-301.
(13) Wilson, G. M.; Johnston, R. H.; Hwang, S. C.; Tsonopoulos, C. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 94-104.
(14) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. *AIChE J.* **1973**, *19*, 238-244.
(15) Van Ness, H. C.; Mrazek, R. V. *AIChE J.* **1959**, *5*, 209.
(16) Van Ness, H. C. *Chem. Eng. Sci.* **1959**, *11*, 118.
(17) Daubert, T. E.; Danner, R. P. *Data Compilation Tables of Properties of Pure Compounds*; Design Institute for Physical Property Data, AIChE, Aug. 1983.

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Liquid–Liquid Equilibria for the System Water–*tert*-Butyl Alcohol–Diisobutylene at 25, 45, and 75 °C

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Liquid–liquid equilibria for the system water–*tert*-butyl alcohol–diisobutylene have been measured at 25, 45, and 75 °C. The experimental data presented in this paper are correlated in terms of the NRTL and UNIQUAC models, and the relevant parameters are presented.

Introduction

tert-Butyl alcohol containing some water is dehydrated to isobutylene in the presence of sulfuric acid or other acid-acting catalyst such as sulfonic acid type cation-exchange resins. When an acid catalyst is applied to *tert*-butyl alcohol, two reactions are catalyzed, dehydration and polymerization. However, a small amount of diisobutylene (2,4,4-trimethyl-1-pentene) is produced in most dehydration processes. It is therefore necessary to separate an aqueous phase containing *tert*-butyl alcohol from an organic phase containing diisobutylene. In the present study, the liquid–liquid equilibria for the ternary system water–*tert*-butyl alcohol–diisobutylene were measured at three different temperatures, 25, 45, and 75 °C, and correlated with the NRTL and UNIQUAC models.

Experimental Section

Chemicals. Diisobutylene (Wako Pure Chemical Industries, Ltd.) and *tert*-butyl alcohol (Junsei Chemical Co., Ltd.) were of guaranteed reagent grade and were used directly without any further purification. The certified minimum purities of these chemicals were 99.5 mol %. A chromatographic analysis on them showed major peak areas of more than 99.9%. Water was deionized and distilled in an all-glass distillation unit prior to use.

Procedure. The experimental work was carried out using screw-capped Pyrex glass tubes similar to that described by Alonso and Recasens (*1*). Each sample tube was 1.5 cm i.d. and 16 cm long. It contained about 20 cm^3 liquid and 8 cm^3 gas-phase (air and solution vapor). The equilibrium cells containing different mixtures of the three components were placed in a thermostated shaking bath operated at 130 rpm (Taiyo incubator M-1). Temperature was controlled within an accuracy of 0.2 °C by using a temperature regulator. After 2 h, the shaker was stopped and the samples were allowed to settle for a period of 5 h. Once equilibrium had been reached, samples of both phases were then taken with long-needled syringes and rapidly injected into a gas chromatograph (Shimadzu GC-9A) equipped with a thermal conductivity detector (100 mA) and connected to an integration unit (Shimadzu C-R3A). Samples of known composition were injected to determine the chromatographic factors for calibration. Chromatographic analyses were performed by injecting 1-μL samples. Special care was

Table I. Experimental Equilibrium Data for the System Water (1)–*tert*-Butyl Alcohol (2)–Diisobutylene (3)

temp, °C	aqueous phase		organic phase	
	x_1	x_2	x_1	x_2
25	0.9807	0.0192	0.0012	0.0387
	0.9731	0.0267	0.0030	0.1208
	0.9638	0.0359	0.0625	0.2003
	0.9581	0.0416	0.0780	0.2953
	0.9535	0.0462	0.1483	0.3817
	0.9490	0.0507	0.2228	0.4155
	0.9447	0.0550	0.3209	0.4313
	0.9406	0.0590	0.4518	0.4108
	0.9275	0.0718	0.5824	0.3474
45	0.9845	0.0154	0.0263	0.0525
	0.9769	0.0230	0.0267	0.1412
	0.9720	0.0279	0.0581	0.2361
	0.9678	0.0321	0.1127	0.3318
	0.9644	0.0354	0.1608	0.3888
	0.9603	0.0396	0.2377	0.4309
	0.9571	0.0427	0.3390	0.4367
	0.9528	0.0470	0.4471	0.4164
	0.9446	0.0550	0.5756	0.3587
75	0.9897	0.0099	0.0114	0.0856
	0.9832	0.0167	0.0489	0.1705
	0.9794	0.0205	0.0676	0.2641
	0.9746	0.0252	0.1187	0.3438
	0.9726	0.0272	0.1606	0.4112
	0.9703	0.0295	0.2462	0.4433
	0.9672	0.0326	0.3267	0.4578
	0.9630	0.0368	0.4251	0.4407
	0.9583	0.0415	0.5504	0.3834

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