Literature Cited

(1) Polak, J.; Liu, B. C. Y. *Can. J. Chem.* **1973**, *51*, 4018–4023.
(2) Helpinstill, J. G.; Van Winkle, M. *Ind. Eng. Chem. Process Des. Dev.* **1968**, *7*, 213–220.
(3) Hildebrand, J. H.; Scott, R. L. *Regular Solutions*; Prentice Hall: Englewood Cliffs, NJ, 1962.
(4) Kabadi, V. N.; Danner, R. P. *Hydrocarbon Process.* **1979**, *58*(5), 245–246.
(5) Price, L. C. *Am. Assoc. Pet. Geol. Bull.* **1976**, *20*, 213–244.
(6) McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267–75.
(7) Mackay, D.; Shiu, W. Y. *Can. J. Chem. Eng.* **1975**, *53*, 239–242.

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Vapor–Liquid Equilibria for *m*-Cresol/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 and quinoline at 250, 275, 300, and 325 °C as well as pure-component vapor pressures. 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 pressures and the VLE measurements, even at extremely low concentrations. The *m*-cresol/quinoline data indicated a high-boiling azeotrope at very low *m*-cresol concentrations that disappeared at higher temperatures.

Introduction

As part of a continuing effort to study the phase behavior of coal-derived liquid model compounds, an equilibrium flash vaporization flow system has been developed (*1*). This system can be used to measure vapor–liquid equilibria (VLE) data at temperatures up to 350 °C and pressures up to 10 MPa and was initially used to study the ethanol/water and the methanol/ethanol systems (*1*).

This equipment has recently been used to generate phase behavior data at 250, 275, 300, and 325 °C for the binary systems of quinoline and *m*-cresol as well as pure-component vapor pressures. These compounds have been selected for two major reasons. Firstly, the compounds are polar and exhibit hydrogen bonding. Thermodynamic research for highly nonideal compounds has been left virtually untouched especially at high temperatures and pressures. Without actual data, proposed equations of state and mixing rules for nonideal systems cannot be tested. Therefore, results of this research will provide basic thermodynamic data for the evaluation and development of models. Secondly, it has been found that the modeling of coal liquids with traditional Kesler–Lee type petroleum correlations (*2*) gives unpredictable results. It has been proposed that the failure of the petroleum correlations for the coal liquids is due to the presence of polar associating compounds in the coal liquids (*3*). *m*-Cresol is considered to be typical of the acidic compounds in coal liquids and quinoline a typical base; consequently, the interactions between *m*-cresol and quinoline may be indicative of the interactions occurring in coal liquids.

A major problem has been encountered in obtaining the VLE data. Since both *m*-cresol and quinoline are capable of hydrogen bonding, they are both quite hygroscopic. Water has been found to be the major impurity and has surprisingly significant effects even at extremely low concentrations. Estimations of the effects of water on our measurements are included in this paper.

Experimental Section

The VLE data were generated on an equilibrium flash vaporization flow system which can operate at temperatures up to 350 °C and pressures up to 10 MPa. A detailed description of the equipment has been previously presented (*1*). The temperature measurements have an estimated accuracy of ±0.1 °C and the pressure measurements are estimated to have an accuracy of ±0.7 kPa below 689.5 kPa and ±3.5 kPa between 689.5 and 3500 kPa. The flow system was particularly advantageous for compounds which decompose at elevated temperatures, since decomposition products tend to be flushed from the equilibrium cell.

The sample analyses were performed on an Hewlett-Packard Model 5710A gas chromatograph with a flame ionization detector (FID). The column chosen was a Hewlett-Packard Series 530 19095S #100 which has a 2.65-μm coating of methylsilicone. The column performed well because it is slightly polar and therefore separates quinoline and *m*-cresol. Each sample was bracketed by two standards so that a relative response factor could be calculated for the sample. With good technique, the accuracy of the 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 chromatograph analysis it was typically found to be 99.8%. However, the water content was difficult to determine below 0.1 wt %. All of the *m*-cresol was distilled in a Perkin Elmer spinning band distillation column to remove the water to the lowest possible level. Vapor pressure measurements agreed with literature values, indicating successful removal of the 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.

Even though the samples were initially purified to 99.9%, the integrity of the samples was monitored while the physical measurements were being made. If decomposition products

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increased to a level above 0.1 area %, the sample was removed from the system. Also, if the pressure measurements appeared to be high, the sample was removed and redistilled to remove water.

Discussion

m-Cresol is a polar compound capable of hydrogen bonding through the hydroxyl group. Based on titration calorimetry data and apparent molecular weight determinations, it has been proposed that *m*-cresol molecules associate with each other in both the dimer and the trimer form (*4*, *5*). The trimer form consists of a six-membered ring of oxygens and hydrogens. This compound is quite hygroscopic due to its hydrogen-bonding capabilities.

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

Due to the hydrogen-bonding capabilities of both compounds, strong intermolecular associations occur between quinoline and *m*-cresol as well as between *m*-cresol molecules. This results in negative deviations from ideality and a high boiling azeotrope at temperatures below 250 °C.

In trying to obtain the VLE data for these compounds a major problem was identified. Initially, the VLE data had a high degree of scatter that could only be attributed to error in the pressure measurements. After carefully checking the actual pressure measurement system and finding no error, the problem was narrowed down to the samples. It was found that both quinoline and *m*-cresol, due to their hygroscopic natures, contain water as purchased even though the manufacturers stated purity was 99+ mol %. It was also found that, if these compounds were exposed to the atmosphere, the water content would increase. Since water has a drastically different vapor pressure than do the compounds of interest, a small amount of water could result in a severe error in the pressure measurements. As discussed below, an attempt was made to estimate effects of trace amounts of water in the samples. It was found that even minute traces had surprisingly significant effects.

Water is a more volatile impurity and will affect the VLE measurements by increasing the measured pressures. The easiest and most accurate way to determine the error due to water on the measurements was to use actual vapor–liquid equilibria experimental data to determine the effects of water on the vapor pressures of the pure compounds. Published VLE data were found for the quinoline/water binary data at atmospheric pressure (*6*). While suitable data were not found for the *m*-cresol/water system, phenol/water binary data were available at atmospheric pressure (*7*). Since *m*-cresol and phenol are similar in molecular structure and chemistry we would expect that using an activity coefficient for water/phenol would give a reasonable approximation for the activity coefficient for water/*m*-cresol.

Using the binary VLE data, an infinite dilution activity coefficient was estimated to be 0.24 for water in quinoline and 4.71 for water in phenol at atmospheric pressure. Assuming that the activity coefficient was independent of temperature (not necessarily a good assumption, but the best that can be done with a limited amount of data) the effects of trace amounts of water on the vapor pressures of quinoline and phenol were estimated. The results of these calculations are shown in Table I. As can be seen, the effects of water on these compounds can be very significant. Assuming a purity of 99.9% quinoline (with the remainder assumed to be water), the error in the pressure measurement ranges from 4.4% (6 kPa) at 250 °C to 3.3% (17.3 kAp) at 325 °C and for 99.99 wt % quinoline the error is 0.43% (0.6 kPa) at 250 °C and 0.33% (1.7 kPa) at 325 °C. For 99.9 wt % *m*-cresol (using water/phenol data) the error is much greater, 58% (175 kPa) at 250 °C to 42% (476.1 kPa) at 325 °C. In fact, for *m*-cresol, the error was so large that the estimated *m*-cresol purity level was increased to 99.99 wt %. At 99.99 wt % *m*-cresol a 3.7% (11.5 kPa) error occurs at 250 °C and a 3% (34.4 kPa) error at 328 °C. These results were quite surprising but completely explained the discrepancies in the data of this investigation and the scatter in literature values for the pure-component vapor pressures of quinoline and *m*-cresol.

Table I. Error in Pressure Measurement Due to Water Contamination

	quinoline	
temp °C	99.9%[a]	99.99%
250	4.4% (6.0)[b]	0.43% (0.6)
275	4.0% (8.8)	0.39% (0.8)
300	3.6% (12.5)	0.35% (1.2)
325	3.3% (17.3)	0.33% (1.7)
	m-cresol (phenol)	
	99.9%	99.99%
250	58.0% (175.5)	3.7% (11.5)
275	51.0% (250.7)	3.4% (17.1)
300	45.8% (349.4)	3.2% (24.6)
325	41.7% (476.1)	3.0% (34.4)

[a] Weight percent. [b] Figures in parentheses are in kilopascals.

Table II. *m*-Cresol Vapor Pressures

temp, K	press., kPa	temp, K	press., kPa
511.2	239.2	565.8	680.8
516.2	265.8	569.1	722.2
522.2	301.3	573.2	771.5
527.4	336.1	592.8	1051.4
545.1	473.3	595.2	1090.4
548.2	500.5	598.1	1141.1
552.4	541.6		

Table III. Quinoline Vapor Pressures

temp, K	press., kPa	temp, K	press., kPa
535.8	175.0	598.2	520.1
536.0	176.0	598.6	523.1
545.0	209.1	603.2	562.4
548.3	223.6	606.5	592.7
556.0	256.7	610.0	622.4
573.7	350.5	612.7	649.6
575.8	362.2	614.4	664.5
589.8	454.9	618.4	709.3
597.6	515.6	619.7	721.4

Figure 1 shows a plot of *m*-cresol vapor pressures from several sources. (*8*, *13*) The data reported by Nasir et al. (*8*) are consistently higher than the rest of the data in Figure 1. As stated in their article, the *m*-cresol was used as purchased from Aldrich with no further purification. The data of Nasir are approximately 50 kPa higher than the rest of the data at 325 °C; this error may result from a trace amount of water. A water concentration as low as 0.02 wt % could be the reason for the discrepancy in vapor pressure measurements.

It can be seen that when dealing with compounds that are capable of hydrogen bonding and consequently are hygroscopic, a tremendous effort must be made to not only purify the samples but also to isolate them from the atmosphere before and during the actual physical measurements.

Experimental Results

Vapor Pressure Measurements. Vapor pressure measurements were generated for *m*-cresol and quinoline over the

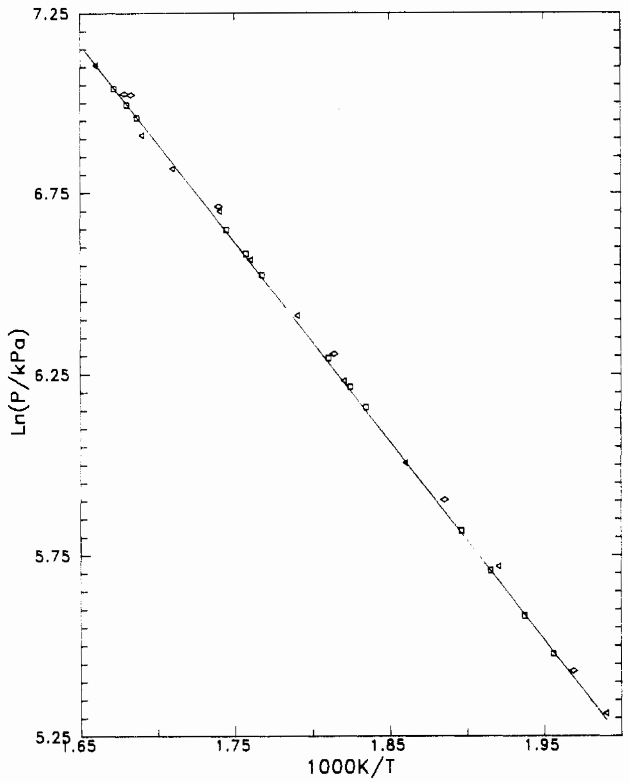

Figure 1. *m*-Cresol vapor pressure comparisons: □, this investigation; △, Glaser (*13*); ◇, Nasir (*8*).

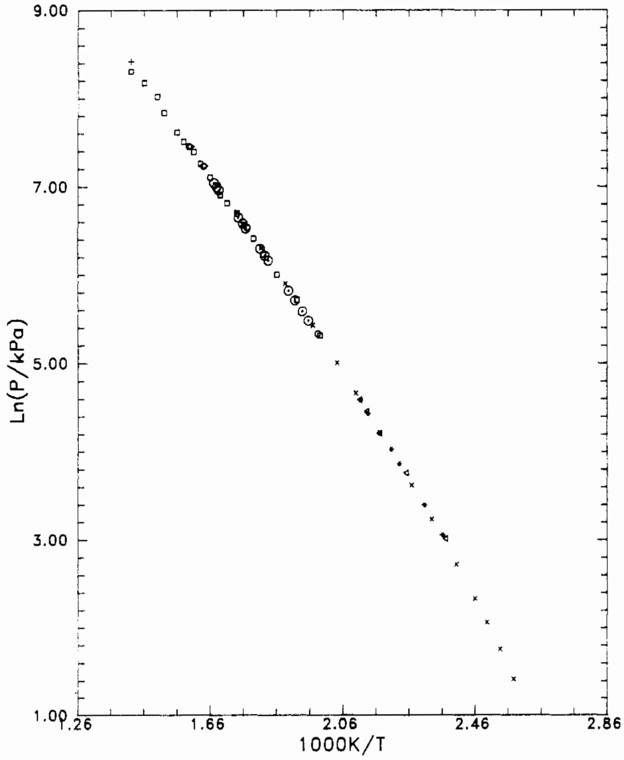

Figure 2. *m*-Cresol vapor pressures: ○, Flanigan (*9*); □, Glaser (*13*); △, Goldblum (*14*); ◇, Cerise (*15*); +, Reid (*10*); ×, Nasir (*8*); ⊙, this investigation; *, Krevor (*12*).

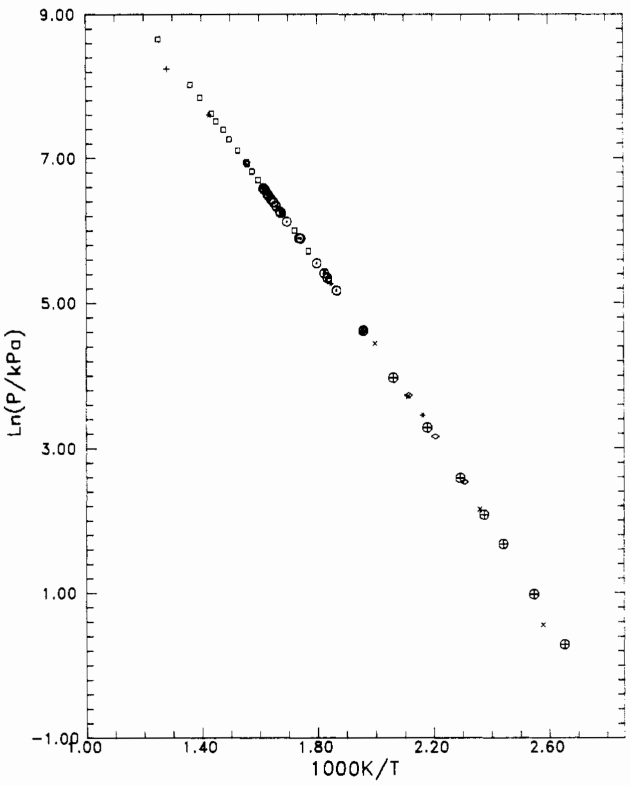

Figure 3. Quinoline vapor pressures: ○, Flanigan (*9*); □, Glaser (*13*); △, Cerise (*15*); ◇, Krevor (*12*); +, Lin (*16*); ×, Nasir (*8*); *, Sebastian (*17*); ⊕, Stull (*18*); ⊙, this investigation.

temperature range of 250–325 °C. These measurements are presented in Tables II and III. In Figures 2 and 3, the data from this research are compared with published data (*8*, *10*, *12*–*18*) and vapor pressure data generated at the Colorado School of Mines on a flow calorimeter (*9*).

In both figures it can be seen that there are discrepancies in the literature data. Based on the previous discussion, it is believed that these discrepancies are most likely due to trace amounts of water. The data from this investigation agree well with a large percentage of the published data and agree very well with the vapor pressure data from the flow calorimeter at the Colorado School of Mines.

It can also be seen in Figures 2 and 3 that there are discrepancies in the published critical points of both compounds. Since the critical properties are quite high for these compounds, they are difficult to measure especially since these compounds tend to decompose at high temperatures. The critical values used in this research were selected based on the ln P versus $1/T$ plots shown in Figures 2 and 3. The published values of the critical properties that best coincided with vapor pressure data were chosen. The critical properties used for *m*-cresol were T_c = 705.8 K and P_c = 4560 kPa. For quinoline the critical properties used were T_c = 800.2 and P_c = 5775 kPa. Acentric factors were calculated for each compound by fitting the vapor pressure data close to T_r = 0.7 to a polynomial and predicting the vapor pressure at T_r = 0.7. The calculated acentric factor for *m*-cresol was 0.452 as compared to a published value of 0.464 (*10*). The calculated acentric factor for quinoline was 0.316 which agrees with the published value, (*10*).

***Vapor–Liquid Equilibria Measurements*.** Listed in Tables IV and V and shown in Figures 4 and 5 are the binary VLE data for the *m*-cresol/quinoline system at four isotherms, 250, 275, 300, and 325 °C. At the lowest isotherm, 250 °C, a high boiling azeotrope may be present at a low *m*-cresol concentration. Due to difficulties with water contamination it is difficult to determine exactly where the azeotrope occurs. Literature data (*11*) and (*12*) indicate the presence of an azeotrope at temperatures between 160 and 200 °C that occurs at increasingly lower concentrations of *m*-cresol as the temperature increases.

A small degree of scatter is present in the *Pxy* plot of the VLE data. In Figure 6 typical *x*–*y* data are plotted for the 275 °C isotherm. It can be seen that a smooth curve is formed

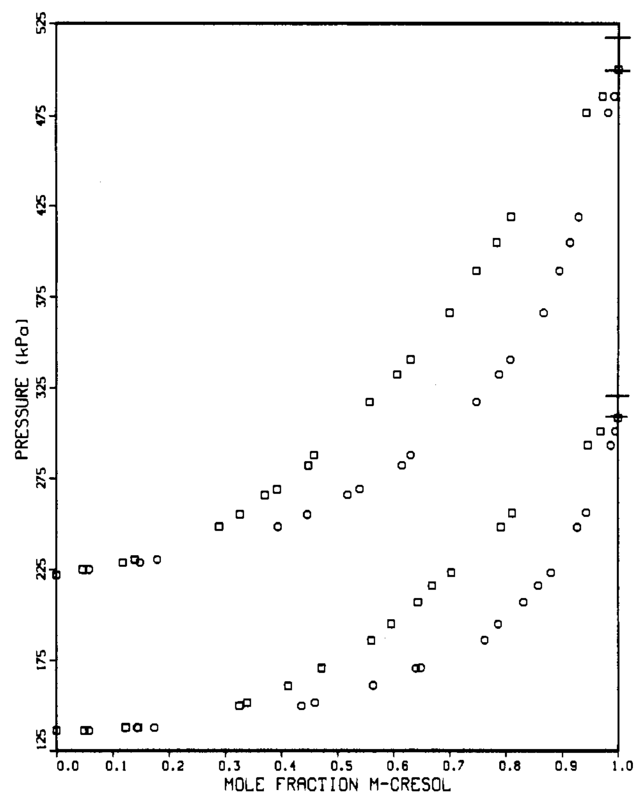

Figure 4. *m*-Cresol/quinoline VLE data at 250 and 275 °C: □, liquid and ○, vapor.

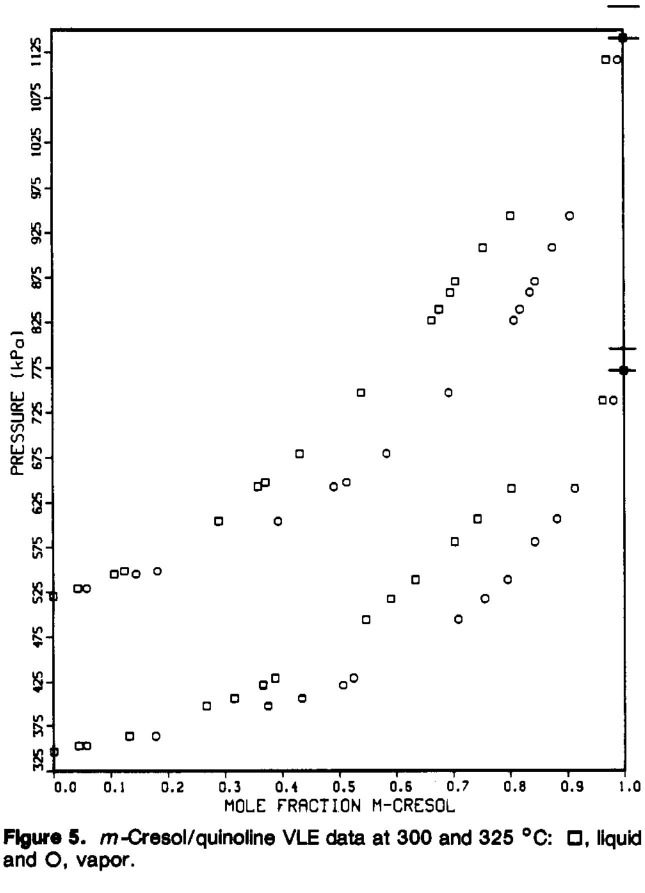

Figure 5. *m*-Cresol/quinoline VLE data at 300 and 325 °C: □, liquid and ○, vapor.

Table IV. VLE Measurements for *m*-Cresol (1)/Quinoline (2)

temp, °C	press., kPa	mol % *m*-cresol		γ_1[a]	γ_2[a]	G^E/RT
		x	y			
250	134.6[b]	0.0	0.0			
	136.2	4.9	5.8	0.545	1.006	−0.024
	137.9	12.3	14.3	0.542	1.005	−0.071
	137.8	14.5	17.4	0.559	0.993	−0.091
	150.0	32.5	43.5	0.677	0.933	−0.174
	151.6	33.9	45.9	0.692	0.922	−0.179
	161.1	41.2	56.3	0.741	0.887	−0.194
	170.7	47.1	63.9	0.777	0.861	−0.198
	171.0	47.1	64.8	0.789	0.841	−0.203
	186.1	56.0	76.2	0.847	0.741	−0.225
	195.1	59.5	78.6	0.860	0.757	−0.202
	207.0	64.3	83.1	0.890	0.718	−0.193
	216.2	66.8	85.8	0.922	0.676	−0.185
	223.3	70.3	88.0	0.926	0.658	−0.178
	248.4	79.1	92.7	0.958	0.629	−0.131
	256.1	81.1	94.3	0.979	0.559	−0.128
	293.3	94.6	98.7	0.996	0.506	−0.040
	301.0	96.9	99.5	1.004	0.347	−0.029
	308.3	100.0	100.0			
275	221.9	0.0	0.0			
	225.1	4.7	5.8	0.590	1.002	−0.023
	228.9	11.8	14.8	0.609	0.995	−0.063
	230.4	13.9	17.9	0.629	0.988	−0.075
	248.6	28.9	39.3	0.714	0.951	−0.133
	255.3	32.6	44.6	0.737	0.938	−0.142
	265.9	37.1	51.7	0.780	0.911	−0.151
	269.0	39.2	53.9	0.778	0.909	−0.156
	282.1	44.8	61.5	0.812	0.875	0.167
	287.9	45.8	63.0	0.830	0.872	−0.160
	317.1	55.7	74.8	0.886	0.795	−0.169
	332.3	60.6	78.8	0.896	0.786	−0.161
	340.5	63.0	80.8	0.904	0.775	−0.158
	366.4	70.0	86.7	0.934	0.708	−0.151
	389.6	74.7	89.5	0.956	0.700	−0.123
	405.1	78.3	91.4	0.965	0.693	−0.107
	419.0	80.9	92.9	0.979	0.670	−0.093
	477.1	94.3	98.1	0.997	0.675	−0.025
	486.1	97.2	99.2	0.994	0.588	−0.020
	500.5	100.0	100.0			

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

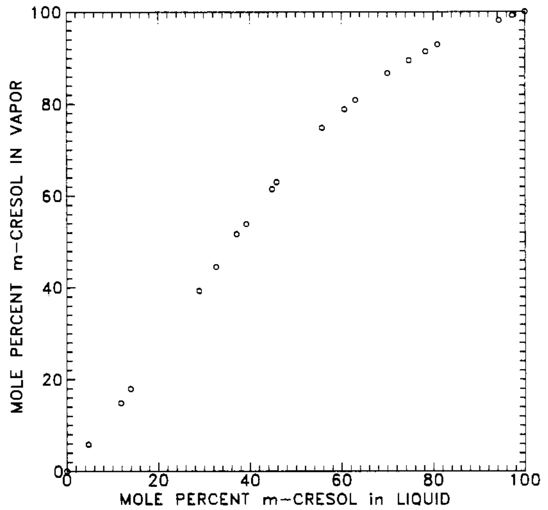

Figure 6. *XY* plot for *m*-cresol/quinoline VLE data at 275 °C.

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 obtained. Therefore, it appears that the system was at equilibrium and scatter in the *Pxy* plot is either due to error in the temperature or pressure measurements. Because of the water contamination problem, it is believed that the scatter is due to trace amounts of water resulting in uncertainties in the pressure. Figures 4 and 5 have two marks at 100% *m*-cresol for each isotherm. The distance between the two marks is the error that would result from a 0.01 wt % water contaminations as presented in Table I. It

Table V. VLE Measurements for *m*-Cresol (1)/Quinoline (2)

temp, °C	press., kPa	mol % *m*-cresol				
		x	y	$\gamma_1{}^a$	$\gamma_2{}^a$	G^E/RT
300	346.2	0.0	0.0			
	353.0	4.4	5.8	0.652	1.003	−0.019
	363.4	13.2	17.8	0.685	0.991	−0.058
	397.2	26.7	37.5	0.775	0.968	−0.092
	406.0	31.6	43.4	0.773	0.958	−0.110
	421.4	36.6	50.6	0.805	0.934	−0.123
	429.4	38.7	52.5	0.804	0.945	−0.119
	494.6	54.7	70.8	0.872	0.893	−0.126
	517.4	59.0	75.5	0.898	0.861	−0.124
	538.8	63.3	79.5	0.914	0.835	−0.123
	581.2	70.3	84.3	0.933	0.845	−0.099
	606.8	74.3	88.2	0.960	0.762	−0.100
	640.8	80.2	91.3	0.965	0.764	−0.081
	738.4	96.2	98.2	0.978	0.945	−0.024
	738.4	96.2	98.1	0.977	0.968	−0.024
	771.5	100.0	100.0			
325	520.4	0.0	0.0			
	529.2	4.2	5.8	0.716	0.998	−0.016
	545.3	10.6	14.4	0.724	0.999	−0.036
	548.6	12.4	18.1	0.782	0.980	−0.048
	604.3	28.9	39.3	0.795	0.976	−0.084
	643.2	35.8	49.1	0.847	0.957	−0.087
	647.6	37.1	51.3	0.859	0.940	−0.095
	679.8	43.1	58.3	0.877	0.929	−0.098
	747.0	53.9	69.2	0.904	0.918	−0.094
	827.0	66.3	80.7	0.935	0.858	−0.096
	839.5	67.6	81.8	0.942	0.852	−0.092
	858.4	69.6	83.5	0.951	0.839	−0.088
	870.7	70.5	84.4	0.961	0.827	−0.084
	908.4	75.3	87.5	0.966	0.819	−0.075
	943.9	80.2	90.6	0.970	0.793	−0.071
	1117.1	97.0	99.0	1.004	0.636	−0.010
	1141.1	100.0	100.0			

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

is obvious that the error due to water contamination is significant.

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. 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

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

where γ_i is the activity coefficient, y_i and x_i are vapor and liquid mole fractions, P is the system pressure, $P_{i,\mathrm{sat}}$ is saturation vapor pressure of pure i, $(\hat{\phi}_L{}^{\mathrm{V}}/\phi_{i,\mathrm{sat}})$ is the vapor-phase correction for nonidealities, $(\hat{f}_i{}^{\mathrm{L}*}/\hat{f}_i{}^{\mathrm{L,P}})$ is the correction of the nonisobaric activity coefficients to constant pressure, and $(f_i{}^{*}/f_{i,\mathrm{sat}})$ is the Poynting correction term. The fugacity coefficients were calculated from an equation of state. The excess Gibbs free energy (G^E/RT) was calculated by using eq 2. The activity coefficients as well as the excess Gibbs free energy are listed in Tables IV and V. The activity coefficients are less than 1.0 and approach 1.0 as the temperature increases, indicating that at higher temperatures the binary system becomes more ideal. Figure 7 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 275 °C isotherm. It is believed that the scatter is due to vapor pressure variations resulting from sample impurities, particularly water. A thermodynamic consistency test (as described by Niesen et al. (*1*)) was performed using the calculated activity coefficients. The data appear to be consistent between 0.1 and 0.9 mole fraction *m*-cresol. At very low and very high *m*-cresol concentrations this thermodynamic consistency test is extremely sensitive to small deviations in the liquid-phase concentrations; consequently, the data in these regions cannot be tested for consistency.

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

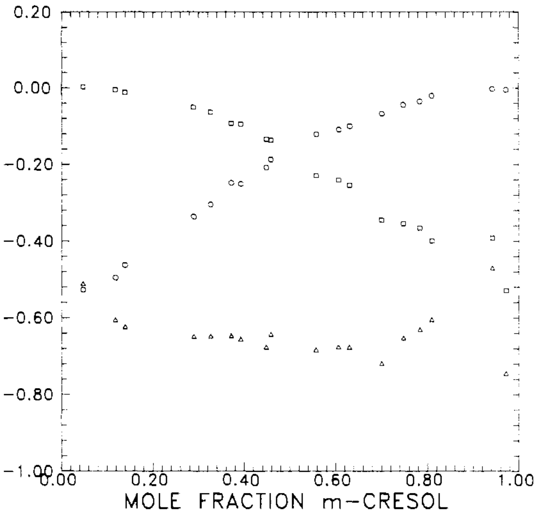

Figure 7. Activity coefficients and excess gibbs free energies for the *m*-cresol/quinoline system at 275 °C: ○, ln γ_1; □, ln γ_2; △, $\Delta G^E/RTx_1x_2$.

Conclusions

Binary phase behavior data and pure-component vapor pressure data were obtained for the compounds *m*-cresol and quinoline at four isotherms, 250, 275, 300, and 325 °C. The *m*-cresol/quinoline binary exhibits a high boiling azeotrope that disappears with increasing temperature. Vapor pressure measurements for these compounds agreed well with most published values as well as vapor pressures from a complementary calorimetry program also at the Colorado School of Mines, (*9*).

In the process of obtaining these data a major difficulty was identified, which is the drastic effect that minute traces of water can have on these measurements. When working with polar, hydrogen-bonding compounds, extreme care must be taken to remove all water and to isolate the samples from the atmosphere.

Glossary

γ	activity coefficient
ϕ	fugacity coefficient
f	fugacity
x	liquid phase mole fraction
y	vapor phase mole fraction
P	pressure
R	gas constant
T	temperature
G^E	excess Gibbs free energy
^	applies to components in a mixture

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

Literature Cited

(1) Niesen, V. G.; Palavra, A.; Kidnay, A. J.; Yesavage, V. F. *Fluid Phase Equilib.* **1986**, *31*(3), 283–298.
(2) Kesler, M. G.; Lee, B. I. *Hydrocarbon Process.* **1976**, *55*(3), 153.
(3) Sharma, R. Ph.D. Thesis 2318, Colorado School of Mines, 1980.
(4) Eatough, D. J.; Wolfley, S. L.; Dungan, L. J.; Lewis, E. A.; Hansen, L. D. *Energy Fuels*, submitted for publication.
(5) Sandarusi, J. M.S. Thesis 2859, Colorado School of Mines, 1984.
(6) Maczynski, A.; Maczynska, Q. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1965**, *13*, 299.
(7) Brusset, H.; Gaynes, J. *Compt. Rend.* **1953**, *236*, 1563.
(8) Nasir, P.; Hwang, S. C.; Kobayashi, R. *J. Chem. Eng. Data* **1980**, *25*, 298.
(9) Flanigan, D. A. Ph.D. Thesis 3305, Colorado School of Mines, 1986.

(10) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
(11) Lekhova, G. B.; Kushner, T. M.; Kharlampovick, G. D.; Serafimov, L. A. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1971**, *45*, 11.
(12) Krevor, D. H.; Lam, F. W.; Prausnitz, J. M.; *J. Chem. Eng. Data* **1986**, *31*, 353-357.
(13) Glaser, F.; Ruland, H. *Chem.-Ing.-Tech.* **1957**, *12*, 772.
(14) Goldblum, K. F.; Martin, R. W.; Young, R. B. *Ind. Eng. Chem.* **1947**, *39*, 1471.
(15) Cerise, K. M.S. Thesis 2623, Colorado School of Mines, 1980.
(16) Lin, C. T.; Young, F. K.; Brule, M. R.; Lee, L. L.; Starling, K. E.; Chao, J. *Hydrocarbon Process.* **1980**, *59*, 117.
(17) Sebastian, H. M.; Simnick, J. J.; Lin, H.; Chao, K. *J. Chem. Eng. Data* **1978**, *23*, 305.
(18) Stull, D. R. *Ind. Eng. Chem.* **1947**, *39*, 517.

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Solubility of Carbon Dioxide, Methane, and Ethane in *n*-Octacosane

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Solubility of carbon dioxide, methane, and ethane in *n*-octacosane has been measured in a semiflow apparatus over the temperature range of 100–300 °C and pressure from 10 to 50 atm. Henry's constant and partial molar volume at infinite dilution are determined from the solubility data.

Introduction

This article reports data from an investigation of gas solubilities in wax slurry for Fischer–Tropsch synthesis reactors. Solubility of carbon dioxide, methane, and ethane in *n*-octacosane (n-C_{28}) has been determined over the temperature range of 100–300 °C and pressure from 10 to 50 atm. Henry's constant and partial molar volume at infinite dilution of the dissolved gases are obtained by fitting the Krichevsky–Kasarnovsky equation to the data.

Experimental Section

A semiflow apparatus has been designed and constructed for the measurement of gas solubilities in molten waxes. Detailed description of the equipment and operation procedure has been reported (*1*). In the course of an experiment, the molten wax was kept in a presaturator and an equilibrium cell, which were housed in series in a thermostated nitrogen bath. A gas stream continuously sparged through the cells. Upon saturation, liquid samples from the equilibrium cell were withdrawn, reduced in pressure, and collected in a trap. The condensed wax was weighed with an analytical balance, and the liberated gas from the trap was measured volumetrically in a buret. The temperature of the equilibrium cell contents was measured to ±0.1 °C by a calibrated type K chromel–alumel thermocouple. Pressure was measured by a Heise gauge to ±0.05 atm.

The gases were purchased from Matheson Gas Products with a minimum purity of 99.8% for carbon dioxide and 99% for methane and ethane. The *n*-octacosane was purchased from Alfa Products, Morton Thiokol, Inc., with a minimum purity of 99%.

Possible thermal degradation of the wax during the experiment was examined by gas chromatographic (GC) analysis of the wax and by comparing repeated data points. The GC patterns of fresh and used waxes did not show any differences, and solubility data were reproducible within experimental errors regardless of the age of wax in operation.

Table I. Carbon Dioxide (CD) + *n*-Octacosane VLE Data

t, °C	P, atm	x_{CD}	y_{CD}	K_{CD}
100.2	10.05	0.102		9.84
	20.14	0.184		5.44
	30.01	0.254		3.93
	40.15	0.324		3.09
	49.90	0.379		2.64
200.3	9.87	0.0688		14.5
	20.04	0.135		7.39
	30.18	0.194		5.14
	39.89	0.247		4.05
	49.95	0.293		3.42
300.3	9.81	0.0596	0.9957	16.7
	20.06	0.122	0.9975	8.16
	30.08	0.176	0.9981	5.69
	39.92	0.226	0.9983	4.42
	49.91	0.270	0.9983	3.69

Table II. Methane (M) + *n*-Octacosane VLE Data

t, °C	P, atm	x_M	y_M	K_M
100.1	9.77	0.0566		17.7
	19.90	0.113		8.87
	30.04	0.163		6.13
	40.19	0.204		4.90
	49.97	0.244		4.11
200.2	9.78	0.0496		20.2
	19.81	0.100		10.00
	29.88	0.143		6.99
	40.36	0.189		5.30
	49.95	0.224		4.46
300.1	9.48	0.0493	0.9962	20.2
	19.74	0.102	0.9979	9.78
	30.21	0.152	0.9985	6.57
	40.17	0.195	0.9986	5.12
	50.11	0.230	0.9986	4.34

Table III. Ethane (E) + *n*-Octacosane VLE Data

t, °C	P, atm	x_E	y_E	K_E
100.1	9.76	0.180		5.54
	19.90	0.322		3.11
	28.82	0.425		2.35
	40.18	0.504		1.98
200.1	9.82	0.113		8.85
	19.87	0.207		4.83
	29.81	0.287		3.48
	37.46	0.335		2.99
300.0	9.62	0.0840	0.9957	11.9
	19.76	0.166	0.9973	6.00
	29.83	0.236	0.9976	4.24
	39.87	0.297	0.9977	3.36

Results and Discussion

Tables I, II, and III present the solubility, x, in mole fraction, of carbon dioxide, methane, and ethane in *n*-octacosane of this work. Because of the low volatility of *n*-octacosane, the equilibrium gas phase is virtually pure solute at 100 and 200 °C where the gas composition, y, in mole fraction, is not explicitly reported. The gas composition measured at 300 °C is reported

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