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

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Ternary vapor–liquid equilibria at elevated pressures are reported for the *m*-cresol/quinoline/tetralin ternary system at 523.15, 548.15, 573.15, and 598.15 K. These results supplement previously reported results of vapor–liquid equilibrium for the pure fluids and binary mixtures, as well as pure, binary, and ternary measurements of the enthalpy for this ternary system. The system is of interest because the components form highly nonideal mixtures and are also models for coal liquids.

Introduction

This is the last phase of an effort to obtain experimental vapor–liquid equilibrium and enthalpy measurements for the ternary model compound system *m*-cresol/quinoline/tetralin. This system is not only indicative of highly nonideal interactions among polar, nonpolar, and associating species, but is also indicative of interactions likely to be present in coal-derived liquids. Mixtures of *m*-cresol/quinoline/tetralin include interactions among an acidic oxygen compound, a basic nitrogen compound, and a two-ring aromatic hydrocarbon.

Vapor pressures for each of the three pure fluids and vapor liquid equilibria for each of the three binary mixtures have previously been recorded at temperatures between 523 and 598 K(*1, 2*). Furthermore, enthalpy measurements for each of the pure fluids (*3–6*) for mixtures consisting of each of the three binary pairs (*7–9*) and for selected ternary mixtures at temperatures between 291 and 650 K and at pressures to 10 MPa have been reported (*10*). Modern process engineering calculations generally require both phase behavior and enthalpy estimation methods. Generally equation of state methods are used in these calculations. However, these equations are least reliable for mixtures involving highly nonideal systems, such as the one under study. Thus, the data set completed in the present investigation offers a unique and critical test of thermodynamic property correlations.

Experimental Details

A description of the apparatus is presented by Niesen (*11*), who used the equipment for vapor–liquid equilibrium measurements on the binary pairs (*1, 2*). Ternary data, due to the extra degree of freedom, are considerably more difficult to obtain than binary data. The flow system had the advantages of constant flushing of decomposed products from the cell along with the capability of sampling without disturbing the equilibria in the cell. Only the micrometering valve in the constant air bath needed to be made operable to account for the third degree of freedom accompanying the ternary system. The operation of this micrometering valve provided another source for controlling the flow rates leaving the cell. In this way, measurements with both temperature and pressure constant could be made. The estimated experimental accuracy in the temperature measurement is 0.1 K, while the accuracy in the pressure measurements is 0.7 kPa at pressures below 689.5 kPa and 3.5 kPa above 689.5 kPa. Details of the operation of the system for ternary measurements are reported elsewhere (*12*).

The *m*-cresol was purchased from Sigma Chemical Co. with a stated purity of 99%. Synthetic quinoline was purchased from Alfa products with a purity level of 99%, and tetralin was purchased from Aldrich Chemical Co. at a purity of 99%. A final sample purity of >99.9%, as determined by gas chromatography, was achieved by the use of a spinning band distillation column. This purity was maintained for the mixture throughout its lifetime in the system by constant monitoring using gas chromatography. Analytical determination of the sample's composition was also achieved with the use of gas chromatography, using a Hewlett-Packard gas chromatograph (GC), model 5890, with a thermal conductivity detector. The column that was used in this GC was a wide-bore 15-m JW Scientific methylpolysiloxane column. The composition of the samples was determined to within ±0.005 mole fraction. Details are reported elsewhere (*12*). Since these compounds are hygroscopic, the experimental apparatus was isolated from the atmosphere, to prevent absorption of water.

Experimental Results

Vapor–liquid equilibrium data were generated for the ternary system of *m*-cresol, tetralin, and quinoline at four isotherms, 523.15, 548.15, 573.15, and 598.15 K. Three isobars were measured at each isotherm. For the 523.15 K isotherm the isobars measured were 150.0, 200.0, and 275.0 kPa; for the 548.15 K isotherm the isobars measured were 250.0, 325.0, and 425.0 kPa; for the 573.15 K isotherm the isobars measured were 400.0, 480.0, and 650.0 kPa; and for the 598.15 K isotherm the isobars measured were 600.0, 725.0, and 950.0 kPa. The experimental results are presented in Tables I–IV for each isotherm. Three pressures were selected at each isotherm, to span the composition range for each of the three components.

Figures 1 and 2 are typical ternary diagrams for the two temperature extremes. The lines represent polynomial fits of the experimental data. As the pressure increases the composition of quinoline present in the mixture decreases. At the lowest temperature for the lowest pressure investigated, the two-phase region curves to the right, but at the two other pressures the two-phase region curves to the left. This shift in the shape of the two-phase region takes place between the lowest and middle pressures investigated. At the highest temperature all three isobars have the same shape, curving to the left.

Efforts were made to correlate the experimental ternary vapor–liquid equilibrium data by determining equation of state binary interaction parameters and using the results to predict ternary behavior (*13*). Unfortunately, simple mixing

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Table I. VLE Measurements for *m*-Cresol/Tetralin/Quinoline at 523.15 K

X(MC)	*X*(T)	*X*(Q)	*Y*(MC)	*Y*(T)	*Y*(Q)
P = 150 kPa					
0.0000	0.0987	0.9013	0.0000	0.1850	0.8150
0.0770	0.0930	0.8299	0.0857	0.1796	0.7347
0.1650	0.0667	0.7683	0.1942	0.1373	0.6686
0.2196	0.0456	0.7375	0.2589	0.1094	0.6318
0.3210	0.0000	0.6790	0.4305	0.0000	0.5695
P = 200 kPa					
0.0000	0.4638	0.5362	0.0000	0.6000	0.4000
0.0940	0.3638	0.5422	0.1105	0.4888	0.4007
0.2788	0.2103	0.5109	0.3252	0.3247	0.3500
0.4596	0.0943	0.4556	0.5438	0.1552	0.3010
0.6170	0.0000	0.3830	0.8100	0.0000	0.1900
P = 275 kPa					
0.1117	0.8883	0.0000	0.1701	0.8299	0.0000
0.2091	0.6813	0.1096	0.3136	0.6357	0.0507
0.3216	0.5335	0.1413	0.4087	0.5303	0.0610
0.4153	0.4299	0.1553	0.4912	0.4574	0.0514
0.4888	0.3489	0.1623	0.5437	0.3974	0.0590
0.6425	0.1859	0.1716	0.7078	0.2344	0.0578
0.7765	0.0759	0.1476	0.8483	0.1027	0.0489
0.8849	0.0000	0.1151	0.9650	0.0000	0.0350

Table II. VLE Measurements for *m*-Cresol/Tetralin/Quinoline at 548.15 K

X(MC)	*X*(T)	*X*(Q)	*Y*(MC)	*Y*(T)	*Y*(Q)
P = 250 kPa					
0.0000	0.1253	0.8747	0.0000	0.2175	0.7825
0.0846	0.0955	0.8198	0.1056	0.1651	0.7293
0.1926	0.0532	0.7542	0.2469	0.1051	0.6480
0.2999	0.0000	0.7001	0.4100	0.0000	0.5900
P = 325 kPa					
0.0000	0.5099	0.4901	0.0000	0.6310	0.3690
0.0956	0.3912	0.5132	0.1311	0.5016	0.3673
0.2889	0.2059	0.5052	0.3574	0.3123	0.3303
0.3393	0.1596	0.5012	0.4228	0.2529	0.3242
0.3793	0.1250	0.4957	0.4771	0.2049	0.3179
0.5807	0.0000	0.4193	0.7700	0.0000	0.2300
P = 425 kPa					
0.0925	0.9075	0.0000	0.1419	0.8581	0.0000
0.1933	0.6781	0.1287	0.2825	0.6450	0.0724
0.3250	0.4950	0.1800	0.4081	0.5009	0.0910
0.4135	0.3907	0.1958	0.4842	0.4285	0.0873
0.4620	0.3412	0.1969	0.5309	0.3840	0.0851
0.6350	0.1579	0.2071	0.7170	0.2068	0.0762
0.8268	0.0000	0.1732	0.9373	0.0000	0.0627

Table III. VLE Measurements for *m*-Cresol/Tetralin/Quinoline at 573.15 K

X(MC)	*X*(T)	*X*(Q)	*Y*(MC)	*Y*(T)	*Y*(Q)
P = 400 kPa					
0.0000	0.1611	0.8389	0.0000	0.2609	0.7391
0.0794	0.1167	0.8038	0.1025	0.2039	0.6935
0.2122	0.0483	0.7395	0.2865	0.0908	0.6227
0.2845	0.0000	0.7155	0.4000	0.0000	0.6000
P = 480 kPa					
0.0000	0.4607	0.5393	0.0000	0.5724	0.4276
0.0999	0.3318	0.5682	0.1256	0.4418	0.4326
0.2460	0.1972	0.5567	0.2960	0.2849	0.4190
0.3464	0.1162	0.5373	0.4215	0.1900	0.3885
0.5155	0.0000	0.4845	0.6800	0.0000	0.3200
P = 650 kPa					
0.1387	0.8613	0.0000	0.2000	0.8000	0.0000
0.2446	0.6541	0.1113	0.3271	0.6185	0.0543
0.3315	0.5028	0.1657	0.4082	0.5047	0.0871
0.4161	0.3940	0.1900	0.4882	0.4205	0.0913
0.5429	0.2400	0.2170	0.6230	0.2732	0.1038
0.6194	0.1749	0.2057	0.6851	0.2130	0.1019
0.8151	0.0000	0.1849	0.9200	0.0000	0.0800

Table IV. VLE Measurements for *m*-Cresol/Tetralin/Quinoline at 598.15 K

X(MC)	*X*(T)	*X*(Q)	*Y*(MC)	*Y*(T)	*Y*(Q)
P = 600 kPa					
0.0000	0.1810	0.8190	0.0000	0.2704	0.7296
0.0767	0.1268	0.7965	0.1010	0.2022	0.6968
0.1951	0.0420	0.7629	0.2678	0.0704	0.6618
0.1953	0.0435	0.7612	0.2646	0.0685	0.6669
0.2758	0.0000	0.7242	0.3800	0.0000	0.6200
P = 725 kPa					
0.0000	0.5400	0.4600	0.0000	0.6325	0.3675
0.0929	0.3905	0.5165	0.1201	0.4749	0.4049
0.2296	0.2193	0.5511	0.2749	0.3183	0.4067
0.3108	0.1450	0.5464	0.3909	0.2158	0.3955
0.3166	0.1441	0.5393	0.3963	0.2161	0.3875
0.3544	0.1097	0.5359	0.4575	0.1663	0.3762
0.5089	0.0000	0.4911	0.6600	0.0000	0.3400
P = 950 kPa					
0.1770	0.8230	0.0000	0.2401	0.7599	0.0000
0.2520	0.6396	0.1083	0.3399	0.6059	0.0542
0.3473	0.4812	0.1715	0.4169	0.4828	0.1002
0.3872	0.4205	0.1923	0.4536	0.4377	0.1088
0.4891	0.2913	0.2196	0.5632	0.3148	0.1220
0.6172	0.1707	0.2121	0.6857	0.2013	0.1139
0.8071	0.0000	0.1929	0.9100	0.0000	0.0900

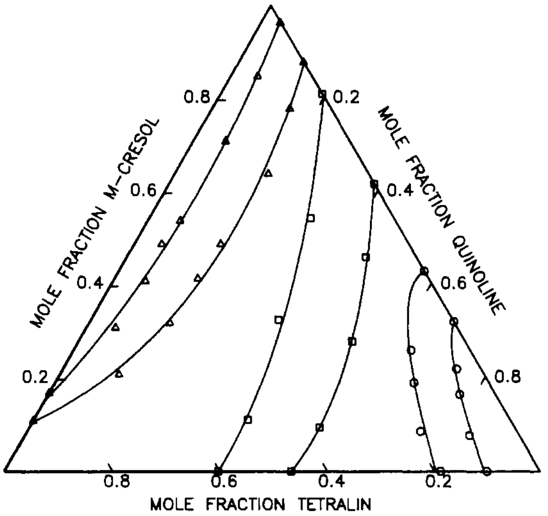

Figure 1. Ternary *m*-cresol/quinoline/tetraline vapor–liquid equilibrium at 523.15 K: ○, 150 kPa; □, 200 kPa; △, 275 kPa.

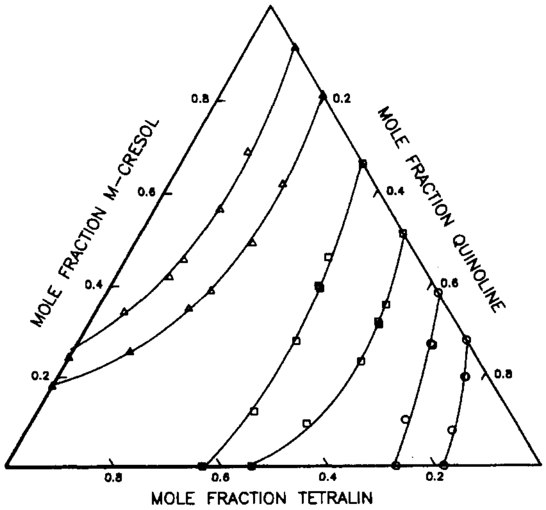

Figure 2. Ternary *m*-cresol/quinoline/tetraline vapor–liquid, equilibrium at 598.15 K: ○, 600 kPa; □, 725 kPa; △, 950 kPa.

rules with traditional equations of state of the van der Waals type did not quantitatively fit the binary vapor–liquid equilibrium data. In order to quantitatively predict the binary data, it was necessary to use a modification of the asymmetric mixing rule of Panagiotopoulos and Reid (*14*). Unfortunately, it has been shown that these asymmetric mixing rules are not invariant when applied to multicomponent systems. Thus, the correlation effort could not be viewed as being successful, and the results are not reported.

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