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Vapor–Liquid Equilibrium in Water + *m*-Cresol + Hydrogen Mixtures at High Temperatures and Pressures

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Vapor–liquid equilibrium in ternary mixtures of water + *m*-cresol + hydrogen was investigated, and experimentally observed compositions of the saturated equilibrium gas and liquid phases are reported at three temperatures (462, 544, and 620 K), four pressures (5, 10, 15, and 20 MPa), and water concentrations in the liquid from 2 to 21 mol %.

Introduction

Vapor–liquid equilibrium (VLE) of water is poorly understood in mixtures of water with heavy hydrocarbons especially at elevated temperatures and pressures and in the presence of light gases. In spite of its fundamental interest to the technology of fuels and oils, information on the vaporization equilibrium of water at such conditions is so far not available. We have started an investigation into this phenomenon. In this work we report results of experimental measurement of VLE in mixtures of water + *m*-cresol + hydrogen at temperatures up to 620 K, pressures to 20 MPa, and water concentrations to 21 mol % in the liquid.

VLE of binary mixtures of *m*-cresol + hydrogen have been reported by Simnick et al. (*1*). No report could be found in the literature about the other two related binary mixtures systems at the conditions of this work. Solubility of compressed hydrogen in water has been studied at elevated temperatures by Suciu and Sibbett (*2*), DeVaney et al. (*3*), and Gillespie and Wilson (*4*). The mutual solubility data of *m*-cresol and water at liquid–liquid equilibrium have been summarized at temperatures up to 410 K by Sorensen and Arlt (*5*).

Experimental Section

A flow apparatus was used to produce saturated equilibrium gas and liquid samples while minimizing thermal decomposition at the high temperatures of this investigation. Detailed description of the apparatus and procedure was given by Lin et al. (*6*).

Compositions of both the gas and liquid samples were determined by first measuring the volume of gas collected upon flashing the samples and cooling down to ambient conditions. The collected condensates were weighed with an analytical balance and analyzed with a gas chromatograph (GC) for water

Table I. VLE Data of Water + *m*-Cresol + Hydrogen Mixtures Obtained from a Liquid Feed Mixture of 2 wt % (10.9 mol %) Water + 98 wt % (89.1 mol %) *m*-Cresol

p, MPa	y_H	y_W	y_C	x_H	x_W	x_C	K_H	K_W	K_C
				462.6 K					
5.09	0.9480	0.0365	0.0155	0.0181	0.0602	0.9217	52.4	0.6062	0.0168
10.46	0.9682	0.0237	0.0081	0.0354	0.0691	0.8955	27.4	0.3430	0.0090
15.49	0.9751	0.0190	0.0059	0.0529	0.0767	0.8704	18.43	0.2476	0.0068
20.30	0.9792	0.0157	0.0051	0.0676	0.0801	0.8523	14.49	0.1960	0.0060
				544.4 K					
5.15	0.8521	0.0415	0.1064	0.0254	0.0237	0.9509	33.6	1.749	0.1119
10.43	0.9153	0.0275	0.0572	0.0517	0.0297	0.9186	17.70	0.9257	0.0623
15.19	0.9326	0.0248	0.0426	0.0775	0.0377	0.8848	12.03	0.6582	0.0481
20.23	0.9418	0.0221	0.0361	0.1001	0.0422	0.8577	9.409	0.5237	0.0421
				619.7 K					
10.99	0.7247	0.0616	0.2137	0.0739	0.0374	0.8887	9.807	1.647	0.2405
15.32	0.7857	0.0479	0.1664	0.1096	0.0380	0.8524	7.169	1.261	0.1952
20.29	0.8307	0.0375	0.1318	0.1457	0.0394	0.8149	5.701	0.9514	0.1618

Table II. VLE Data of Water + *m*-Cresol + Hydrogen Mixtures Obtained from a Liquid Feed Mixture of 4 wt % (20.0 mol %) Water + 96 wt % (80.0 mol %) *m*-Cresol

p, MPa	y_H	y_W	y_C	x_H	x_W	x_C	K_H	K_W	K_C
				463.0 K					
5.27	0.9301	0.0545	0.0154	0.0175	0.0984	0.8841	53.2	0.5538	0.0174
10.18	0.9562	0.0358	0.0080	0.0335	0.1146	0.8519	28.5	0.3124	0.0094
15.13	0.9640	0.0302	0.0058	0.0501	0.1340	0.8159	19.24	0.2253	0.0071
20.25	0.9688	0.0263	0.0049	0.0641	0.1454	0.7905	15.11	0.1809	0.0062
				544.0 K					
5.24	0.8265	0.0642	0.1093	0.0242	0.0395	0.9363	34.2	1.623	0.1167
10.41	0.9004	0.0405	0.0591	0.0507	0.0449	0.9044	17.76	0.9026	0.0654
15.54	0.9190	0.0367	0.0443	0.0746	0.0588	0.8666	12.32	0.6237	0.0511
20.44	0.9318	0.0315	0.0367	0.0968	0.0629	0.8403	9.626	0.5008	0.0437
				620.6 K					
10.57	0.6593	0.1178	0.2229	0.0654	0.0716	0.8630	10.08	1.646	0.2583
15.37	0.7446	0.0885	0.1669	0.1002	0.0728	0.8270	7.431	1.216	0.2018
20.35	0.7902	0.0813	0.1285	0.1350	0.0886	0.7764	5.853	0.9171	0.1655

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Table III. VLE Data of Water + *m*-Cresol + Hydrogen Mixtures Obtained from a Liquid Feed Mixture of 8 wt % (34.3 mol %) Water + 92 wt % (65.7 mol %) *m*-Cresol

p, MPa	y_H	y_W	y_C	x_H	x_W	x_C	K_H	K_W	K_C
463.8 K									
5.17	0.8983	0.0867	0.0150	0.0164	0.1632	0.8204	54.8	0.5313	0.0183
10.26	0.9374	0.0547	0.0079	0.0304	0.1863	0.7833	30.8	0.2936	0.0101
15.06	0.9499	0.0445	0.0056	0.0462	0.2007	0.7531	20.6	0.2217	0.0075
20.18	0.9582	0.0371	0.0047	0.0596	0.2119	0.7285	16.08	0.1751	0.0065
544.1 K									
5.22	0.7737	0.1157	0.1106	0.0226	0.0751	0.9023	34.2	1.540	0.1226
10.17	0.8670	0.0703	0.0627	0.0487	0.0816	0.8697	17.80	0.8612	0.0721
15.58	0.8974	0.0573	0.0453	0.0712	0.0977	0.8311	12.60	0.5865	0.0545
20.36	0.9135	0.0494	0.0371	0.0938	0.1037	0.8025	9.739	0.4766	0.0462
618.7 K									
10.36	0.5838	0.1903	0.2259	0.0538	0.1186	0.8276	10.84	1.604	0.2730
15.32	0.6797	0.1584	0.1619	0.0891	0.1452	0.7657	7.628	1.091	0.2115
20.39	0.7290	0.1481	0.1229	0.1219	0.1658	0.7123	5.980	0.8934	0.1725

and *m*-cresol. A temperature programmed Hewlett-Packard GC Model 5710A with a thermal conductivity detector and Porapack Q column was used for the analysis.

Due to the enormous difference in volatilities of hydrogen and the solvents, quantitative separation is obtained at the liquid trap where the heavy components are retained as liquid at ambient conditions. Only minor corrections need to be made to the directly measured liquid weights and gas volumes. To correct for the solvents vaporizing into the collected gas, we assume that the gas behaves ideally at ambient conditions and that the stream is saturated with both water and *m*-cresol. The quantities of solvents vaporized were then calculated from their vapor pressure data. The solubility of hydrogen in mixed solvents is extremely small at room temperatures; no correction is made for the hydrogen dissolved in the condensate.

Concentrations of water in the equilibrium liquid and gas phases was varied by varying the concentration of water in the liquid feed which is a mixture of water and *m*-cresol. Three concentrations of water in the feed were employed: 2, 4, and 8 wt %. These concentrations are below the solubility of water at ambient temperature. The liquid feed was a homogeneous solution.

Concentration of water in some condensate samples exceeded the solubility of water at ambient temperature. A heterogeneous mixture was obtained upon cooling. Such samples were made homogeneous by addition of a weighed amount of pure *m*-cresol. The homogenized sample was analyzed with the GC, and the true concentration was obtained from the GC result by subtracting the added *m*-cresol.

The hydrogen gas was supplied by Airco, Inc., with a minimum purity of 99.95%. *m*-Cresol was purchased from Aldrich Chemical Company as a gold label product with a purity of 99+%. Deionized distilled water was used to make liquid feed mixtures.

Results

Tables I–III present VLE data for water + *m*-cresol + hydrogen mixtures obtained with feed mixtures of 2, 4, and 8 wt %, respectively, of water in *m*-cresol. The tabulated compositions represent average values obtained from multiple samples. At least two samples were taken at each temperature, pressure, and flow conditions. The duplicate samples agree within 2% in mole fraction of hydrogen. GC analysis of water concentration in liquid condensates is generally reproducible within 3%.

The concentration of water in some equilibrium saturated liquids is quite high. The highest observed $x_w = 0.2119$ is found in Table III. This is, however, still below the solubility of water in *m*-cresol at ambient temperature and surely even further below the solubility at the equilibrium temperature. The liquid mixtures of this work are all homogeneous liquids.

Glossary

K	equilibrium vaporization ratio, $K \equiv y/x$
p	pressure, MPa
T	temperature, K
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscripts

C	*m*-cresol
H	hydrogen
W	water

Registry No. H_2, 1333-74-0; *m*-cresol, 108-39-4.

Literature Cited

(1) Simnick, J. J.; Sebastian, H. M.; Lin, H. M.; Chao, K. C. *J. Chem. Thermodyn.* **1979**, *11*, 531.
(2) Suciu, S. M.; Sibbett, W. L. Argonne National Laboratories, Chicago, IL, 1951; ANL-4603; Part II, pp 1–18.
(3) DeVaney, W.; Berryman, J. M.; Kao, P. L.; Eakin, B. "High Temperature V-L-E Measurements for Substitute Gas Components"; Gas Processors Association: Tulsa, Oklahoma, 1978; Research Report-30, Project 735-A.
(4) Gillespie, P. C.; Wilson, G. M. "Vapor-Liquid Equilibrium Data on Water-Substitute Gas Components: N_2-H_2O, H_2-H_2O, CO-H_2O, H_2-CO-H_2O, and H_2S-H_2O"; Gas Processors Association: Tulsa, Oklahoma, 1980; Research Report-41, Project 758-B-79.
(5) Sorensen, J. M.; Arlt, W. "Liquid-Liquid Equilibrium Data Collection"; Chemistry DECHEMA: Frankfurt/Main, Germany, 1979; Vol. V, Part I.
(6) Lin, H. M.; Kim, H.; Leet, W. A.; Chao, K. C. *Ind. Eng. Chem. Fundam.* **1985**, *24*, 260.

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