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Vapor–Liquid Equilibrium of the Methane–Toluene System at Low Temperatures

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Measurements of the bubble-point compositions are reported at 40, 0, −40, and −120 °F. The pressure ranges from 50.0 to 7070 psia. *K* values were evaluated by combining with earlier dew-point data from this laboratory at 40 and 0 °F and from BWRS predictions at −40° and −120 °F. Limited liquid–liquid miscibility at temperatures below the critical temperature of methane was observed. The *P–x* plot shows reverse solubility of methane in the liquid at high pressures resulting in *K* values of methane at lower temperatures crossing over the ones at higher temperatures.

A number of studies of the vapor–liquid equilibrium of the methane–toluene binary system have been reported in the literature. Savvina and Velikovski (*12*) reported some results from 40 to 150 °C with pressures up to the critical at each temperature. Elbishlawi and Spencer (*6*) studied the equilibrium relations at 150 °F from 100 psia up to the critical pressure of the mixture. Chang and Kobayashi (*2*) reported measurements from 0 down to −100 °F with pressures up to 3500 psia. No experimental bubble point data for the methane–toluene system exist for temperatures between 0 and 100 °F and for pressures above 3500 psia at temperatures below 100 °F.

Dew point loci for the methane–toluene system using the elution method were reported by Hwang and Kobayashi (*8*) from this laboratory at 40, 20, and 0 °F and pressures up to 2500 psia.

This study and that by Chang and Kobayashi (*2*) show some discrepancies in both dew points (*8*) and bubble points as shown in Figure 2.

Two liquid phases were observed at temperatures below the critical temperature of methane. An earlier study from this laboratory (*2*) defined the phase behavior.

Experimental Method and Procedure

The recycle equilibrium apparatus is the same as that used by Mraw et al. (*10*) in the methane–carbon dioxide investigation with some modifications. The sampling lines were all heated to above the boiling point of toluene (231.13 °F) at 300 °F to transform and keep the sample in the vapor phase at essentially atmospheric conditions. The precooler was disconnected due to the operation of a closed system in methane–toluene mixtures.

Toluene was charged to the cleaned and evacuated cell first, methane was then added to the desired pressure. Temperature was controlled by applying liquid nitrogen and a heater from the Thermotrol to ±0.02 °F and was determined with a Leeds and Northrup platinum resistance thermometer. A magnetic pump was used to recycle the gas mixture through the liquid at the bottom of the cell until an equilibrium state is reached. It usually took over an hour to reach the equilibrium state, after which at least six analyses were made.

A stirred pot made of stainless steel with a volume of approximately 150 mL was used to homogenize the sample of the liquid phase (as a vapor) by mixing.

The experimental equipment and technique for the dew-point concentration measurements have been reported in earlier publications (*3–5*, *9*) which should be consulted for itemized information.

In the bubble-point concentration investigation, a TRACOR Model 550 gas chromatograph with thermal conductivity detector was used for analysis. The chromatographic column was a 4-ft length of $^1/_8$-in. o.d. stainless steel tubing packed with 80–100 mesh Duropack (OPN/Porasil C). Helium was used as a carrier gas. The flow rate of helium was determined to give maximum response. Sample was introduced into the sample loop and then bubbled through a water column to indicate the flow rate of the sample. The signal from the detector was integrated by an Autolab minigrator and recorded on a Leeds and Northrup strip chart recorder.

The peak areas were calibrated by preparing samples from two metering pumps. A 500-cm^3 pump was used to deliver a certain flow rate of methane and an 8-cm^3 pump was used to deliver a precise quantity of toluene. The two components were then going through a mixing valve and to the sample loop to be analyzed. Samples with methane mole fractions ranging from 5 to 95% were prepared and analyzed. The area ratios were plotted as a function of the mole fraction ratios. In the region of study, this is a linear relation. See Figure 1.

The isotherms were usually investigated in order of decreasing temperature and increasing pressure. Additional points were sometimes taken on later dates to verify the consistency of the measurements.

The pressure in the system was indicated by four (0–1000, 0–3000, 0–6000, 0–10 000 psia) Heise gauges with accuracy of 0.1% of the full scale reading.

Materials Used

Ultra-high-purity methane (99.97 mol % minimum) was purchased from Matheson Gas Products. The research grade (99.94 mol %) toluene used was donated by the Phillips Petroleum Co. All materials were used without further purification.

Error Analysis

The contributing factors of errors are temperature, controlled to ±0.02 °F, pressure, measured by Heise gauges calibrated

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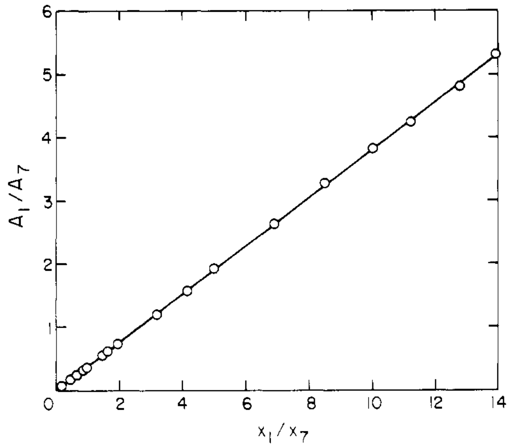

Figure 1. Calibration curve for the methane-toluene system using a T. C. detector.

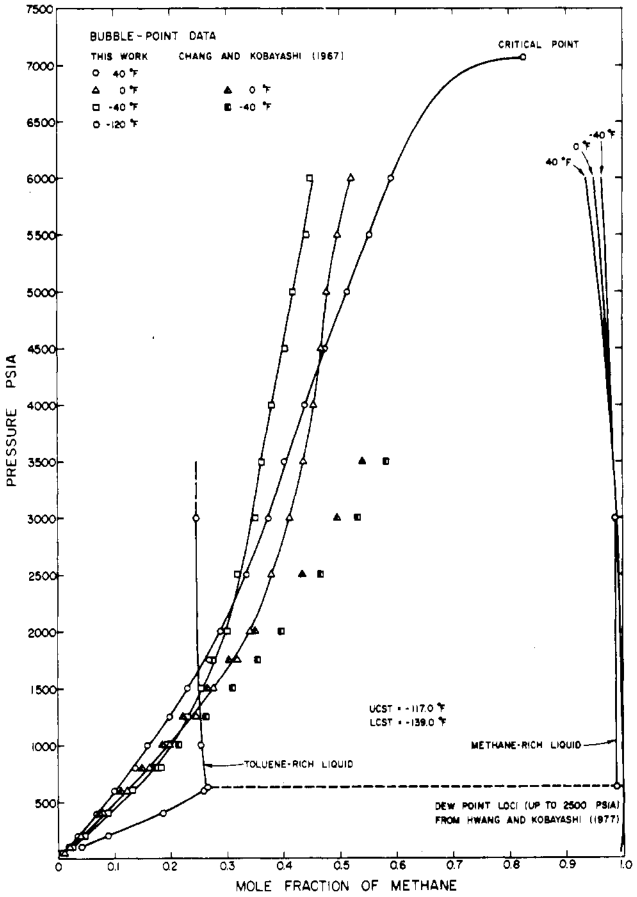

Figure 2. Pressure-composition diagram for the methane-toluene system.

to 0.1% of full scale, concentration, determined by chromatography from peak area ratios calibrated to a maximum error of 2% or 0.005 in mole fraction. The vast majority of the data are valid to four significant figures.

The overall error in the dew point data is either less than 2% or 0.000 05 in mole fraction of toluene depending on which is larger.

Results

Experimental results are shown in Table I. The dew points were measured up to 2500 psia at 40 and 0 °F only; therefore, equilibrium constants K were calculated for each component where data were available. BWRS equation (7) was used to

Table I. Experimental Data of Vapor-Liquid Equilibrium of Methane-Toluene System

P, psia	x methane[b]	y methane	K methane	K toluene
T = 40.00 °F = 4.44 °C				
50.0	0.009669	0.996 13	103.02	0.003 908
100.0	0.01924	0.997 85	51.86	0.002 192
200.0	0.03647	0.996 87	27.33	0.001 380
400.0	0.06838	0.999 105	14.61	0.000 9607
600.0	0.1004	0.999 199	9.952	0.000 8904
800.0	0.1369	0.999 045	7.298	0.001 107
1000.	0.1585	0.998 75	6.301	0.001 485
1250.	0.1980	0.998 30	5.042	0.002 120
1500.	0.2307	0.997 73	4.325	0.002 951
1750.	0.2691	0.996 92	3.705	0.004 214
2000.	0.2881	0.995 81	3.457	0.005 886
2500.	0.3352	0.992 66	2.961	0.011 04
3000.	0.3733			
3500.	0.4015			
4000.	0.4381			
4500.	0.4736			
5000.	0.5130			
5500.	0.5530			
6000.	0.5903			
7070.[a]	0.8259			
T = 0.00 °F = −17.78 °C				
50.0	0.01158	0.999 086	86.28	0.000 9247
100.0	0.02084	0.999 565	47.96	0.000 4443
200.0	0.04147	0.999 710	24.11	0.000 3026
400.0	0.08100	0.999 819	12.34	0.000 1970
600.0	0.1225	0.999 823	8.162	0.000 2017
800.0	0.1622	0.999 767	6.164	0.000 2781
1000.	0.1984	0.999 589	5.038	0.000 5127
1250.	0.2445	0.999 250	4.087	0.000 9927
1500.	0.2763	0.998 77	3.615	0.001 700
1750.	0.3196	0.997 92	3.122	0.003 057
2000.	0.3414	0.996 67	2.919	0.005 056
2500.	0.3782	0.993 51	2.627	0.010 44
3000.	0.4106			
3500.	0.4352			
4000.	0.4532			
4500.	0.4673			
5000.	0.4763			
5500.	0.4960			
6000.	0.5204			
T = −40.00 °F = −40.00 °C				
100.0	0.02531			
200.0	0.04471			
400.0	0.08924			
600.0	0.1326			
800.0	0.1833			
1000.	0.1958			
1250.	0.2300			
1500.	0.2542			
1750.	0.2744			
2000.	0.3003			
2500.	0.3184			
3000.	0.3495			
3500.	0.3613			
4000.	0.3789			
4500.	0.4033			
5000.	0.4170			
5500.	0.4417			
6000.	0.4474			
T = −120.00 °F = −84.44 °C				
100.0	0.04179			
200.0	0.08919			
400.0	0.1861			
600.0	0.2595			
630.0	0.2652 (L_2)			
630.0	0.9898 (L_1)			
1000.	0.2541 (L_2)			
1000.	0.9880 (L_1)			
3000.	0.2459 (L_2)			
3000.	0.9869 (L_1)			

[a] Critical pressure. [b] All liquid-phase data are L_2 unless otherwise noted.

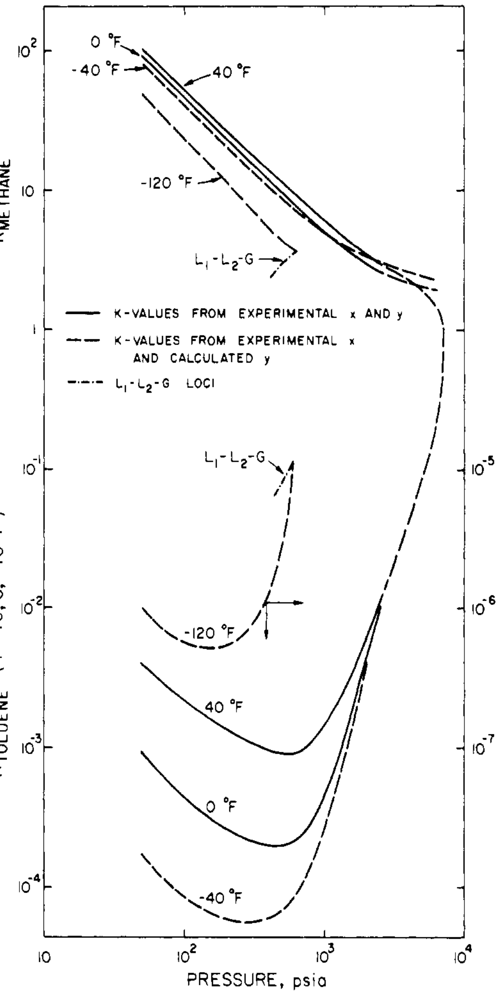

Figure 3. *K* value vs. pressure along isotherms for the methane–toluene system.

generate dew points so that *K* values can be calculated for pressures above 2500 psia and temperatures below 0 °F. These dew points are shown in Table II. The *K* values as a function of pressure are shown in Figure 3.

The pressure–composition behavior is given in Figure 2. Unlike other methane–light hydrocarbon binary systems, the methane compositions in the liquid phase at high pressures are smaller at lower temperatures. That is, the isotherms at low temperatures cross over the isotherms at high temperatures. This is a phenomenon also observed in other systems (*13*).

The phase behavior of methane–toluene as shown in the pressure–temperature projection (Figure 4) has been studied and reported from this laboratory (*2*). Due to the pressure limitation (8000 psia) of the equilibrium cell, critical phenomena of the mixture cannot be observed at temperatures below 40 °F. The critical points at high temperatures were estimated from the vapor–liquid equilibrium data of Savvina and Velokovski (*12*), and Elbishlawi and Spencer (*6*). The critical pressure increases as the temperature decreases. No minimum point in the methane–toluene critical locus is expected as in the system of methane–methylcyclohexane (*1*). Two liquid phases exist between temperatures -117 and -139 °F. The isotherm at -120 °F is in this region. At 630 psia, three phases L_1–L_2–G exist simultaneously. For pressures above 630 psia, only two phases, either L_1 and L_2, or L_1 and G are allowed. L_2 designates toluene-rich liquid and L_1 designates methane-rich liquid.

The comparisons of the bubble-point data of this study and those of Chang and Kobayashi (*2*) are shown in Figure 2. Previous studies by Yarborough (*14*) and Mundis (*11*) indicated that the heptane, methylcyclohexane, and toluene *K* values of Chang and Kobayashi (*2*) are all suspect. This study has confirmed that surmise for the toluene *K* values. The errors in

Table II. BWRS Dew Points and Experimental Bubble Points in the Methane–Toluene System

P, psia	*x* methane	*y* methane	*K* methane	*K* toluene
		$T = 40.00\ °F = 4.44\ °C$		
50.0	0.009 669	0.996 25	103.0	0.003 791
100.0	0.019 24	0.997 93	51.87	0.002 088
200.0	0.036 47	0.998 78	27.38	0.001 268
400.0	0.068 38	0.999 124	14.61	0.000 940 3
600.0	0.100 4	0.999 154	9.952	0.000 940 1
800.0	0.136 9	0.999 074	7.298	0.001 073
1000.	0.158 5	0.998 90	6.302	0.001 294
1250.	0.198 0	0.998 59	5.043	0.001 762
1500.	0.230 7	0.998 10	4.326	0.002 465
1750.	0.269 1	0.997 43	3.707	0.003 510
2000.	0.288 1	0.996 57	3.459	0.004 824
2500.	0.335 2	0.994 29	2.966	0.008 596
3000.	0.373 3	0.991 50	2.656	0.013 60
3500.	0.401 5	0.988 4	2.462	0.019 45
4000.	0.438 1	0.985 1	2.249	0.026 59
4500.	0.4736	0.981 8	2.073	0.034 82
5000.	0.513 0	0.878 4	1.907	0.044 66
5500.	0.553 0	0.975 0	1.763	0.056 33
6000.	0.590 3	0.971 6	1.646	0.069 76
7070.[a]	0.825 9	0.825 9	1.000	1.000
		$T = 0.00\ °F = -17.78\ °C$		
50.0	0.011 58	0.999 142	86.28	0.000 868 1
100.0	0.020 84	0.999 520	47.96	0.000 489 0
200.0	0.041 47	0.999 699	24.11	0.000 314 1
400.0	0.081 00	0.999 759	12.34	0.000 262 4
600.0	0.122 5	0.999 737	8.160	0.000 299 9
800.0	0.162 2	0.999 670	6.164	0.000 394 2
1000.	0.198 4	0.999 550	5.038	0.000 561 6
1250.	0.244 5	0.999 291	4.087	0.000 937 9
1500.	0.276 3	0.998 86	3.615	0.001 578
1750.	0.319 6	0.997 92	3.122	0.003 057
2000.	0.341 4	0.997 37	2.921	0.004 001
2500.	0.378 2	0.995 28	2.632	0.007 592
3000.	0.410 6	0.993 02	2.418	0.011 84
3500.	0.435 2	0.990 68	2.276	0.016 51
4000.	0.453 2	0.988 45	2.181	0.021 12
4500.	0.467 3	0.986 40	2.111	0.025 53
5000.	0.476 3	0.984 34	2.067	0.029 90
5500.	0.496 0	0.982 13	1.980	0.035 46
6000.	0.520 4	0.980 77	1.885	0.040 10
		$T = -40.00\ °F = -40.00\ °C$		
100.0	0.025 31	0.999 918 0	39.51	0.000 084 1
200.0	0.044 71	0.999 944 5	22.37	0.000 058 1
400.0	0.089 24	0.999 947 2	11.21	0.000 058 0
600.0	0.132 6	0.999 929 3	7.541	0.000 081 5
800.0	0.183 3	0.999 886	5.455	0.000 139
1000.	0.195 8	0.999 793	5.106	0.000 258
1250.	0.230 0	0.999 517	4.346	0.000 627
1500.	0.254 2	0.998 97	3.930	0.000 138
1750.	0.274 4	0.998 1	3.637	0.002 62
2000.	0.300 3	0.997 2	3.321	0.004 00
2500.	0.318 4	0.995 3	3.126	0.006 90
3000.	0.349 5	0.993 5	2.843	0.009 99
3500.	0.361 3	0.991 9	2.745	0.012 7
4000.	0.378 9	0.990 4	2.614	0.015 5
4500.	0.403 3	0.989 1	2.452	0.018 3
5000.	0.417 0	0.988 0	2.369	0.020 6
5500.	0.441 7	0.986 9	2.234	0.023 5
6000.	0.447 4	0.986 0	2.204	0.025 3
		$T = -120.0\ °F = -84.44\ °C$		
100.0	0.041 79	0.999 999 46	23.93	0.000 000 564
200.0	0.089 19	0.999 999 51	11.21	0.000 000 540
400.0	0.186 1	0.999 998 95	5.373	0.000 001 29
600.0	0.259 5	0.999 991 70	3.854	0.000 011 2
630.0	0.265 2			
1000.	0.254 1	0.999 948 8	3.935	0.000 068 6
3000.	0.245 9	0.999 868	4.066	0.000 175 7

[a] Critical pressure.

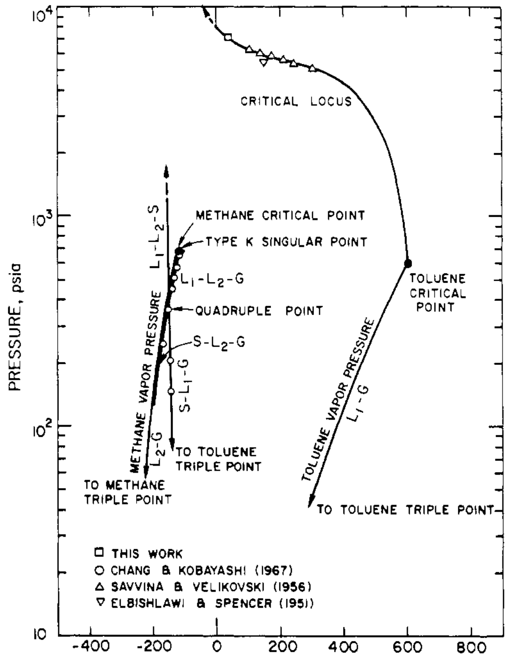

Figure 4. Pressure-temperature projection for the methane-toluene system.

the earlier data by Chang and Kobayashi (*2*) are attributed to sampling and/or analysis.

Acknowledgment

Exxon Production Research Co. provided assistance in yielding the dew points by BWRS predictions. The Phillips Petroleum Co. donated the research grade toluene and the isohexane cryogenic bath fluid. Mr. Ray Martin provided extensive assistance with the experimental apparatus.

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Solubility of Chloromethylmercury(II) and Chloroethylmercury(II) in Water

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The solubilities of chloromethylmercury(II) (MMC) and chloroethylmercury(II) (EMC) in water have been carefully determined between 20 and 40 °C. The temperature dependence of the solubilities expressed as mole fraction, x_2, was given by the following equations: log $x_{2(\mathrm{MMC})} = -1059/T + 0.176$; log $x_{2(\mathrm{EMC})} = -1048/T - 0.612$. The thermodynamic parameters for converting MMC and EMC solids to a saturated aqueous solution were $\Delta\bar{H}_{2(\mathrm{MMC})} = 4711$ cal/mol, $\Delta\bar{S}_{2(\mathrm{MMC})} = 15.8$ eu, $\Delta\bar{H}_{2(\mathrm{EMC})} = 4642$ cal/mol, and $\Delta\bar{S}_{2(\mathrm{EMC})} = 15.6$ eu. The temperature dependence of the partial molal volume, $(\partial^2\bar{V}_2/\partial T^2)_P$, was negative in both MMC and EMC aqueous solutions.

Introduction

It is well known that trace amounts of organic mercury(II) compounds cause serious toxicity in mammals, especially humans. Increasing attention, therefore, is being paid to those compounds found naturally, e.g., in rivers and sea water. Accordingly, attention should be given to any redissolution of the compounds into natural water, for example, after soil reclamation and dredging harbors and contamination by industrial wastes containing an organic mercury(II) compound. For this reason, a fundamental study of the compounds is considered to be urgent for settling these problems.

Although many organic mercury(II) compounds are available, we studied the fundamental properties of MMC and EMC in this experiment, in which MMC is confirmed as the causal agent of so-called "Minamata disease" (*13*-*15*) and is widely analyzed among the organic mercury(II) compounds in natural occurence. EMC was chosen as the most related compound having the same toxicity as MMC.

Several authors have reported studies on the formation of CH_3Hg^+ with several ligands. Waugh et al. (*23*) obtained the solubility product of MMC only at 25 °C from the dissociation constant and solubility in water. Schwarzenbach and Schellenberg (*19*) reported formation constants and the thermodynamic values of CH_3Hg^+ with several ligands, and Budevsky et al. (*4*) studied in detail an interaction of CH_3Hg^+ with Cl^-. Hepler and Olofsson (*11*) also reviewed the thermodynamic properties,