Xylene Azeotropes with 1,1,2,2-Tetrachloroethane

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o-Xylene forms a maximum boiling azeotrope with 1,1,2,2-tetrachloroethane which contains 29.8 wt. % o-xylene and boils at about 147° C. There is also some evidence that *m*-xylene may form an azeotrope with 1,1,2,2-tetrachloroethane which contains about 0.06% *m*-xylene.

A RECENT compilation of azeotropic data (*1*) published by the American Chemical Society quotes from Lecat that no azeotropes are formed from mixtures of 1,1,2,2-tetrachloroethane with either *o*-xylene (*2*) or *m*-xylene (*3*). However, a recent attempt to separate C_8 aromatic isomers in the author's laboratories by azeotropic distillation led to the discovery of a definite maximum boiling azeotrope of the tetrachloroethane with *o*-xylene. Furthermore, there also seems to be a maximum boiling azeotrope of the halocarbon with *m*-xylene although this is not as completely characterized due to the low *m*-xylene concentration in the azeotrope.

EXPERIMENTAL

All of the distillations were made in a 1-inch diameter vacuum jacketed glass distillation column having a 3-ft. packed section of $^{3}/_{16}$-inch Cannon protruded stainless steel packing. This column showed the equivalent of 20 theoretical plates when tested at total reflux with a *n*-heptane–methylcyclohexane test mixture. The distillations were run at a reflux ratio of 5:1 as determined by the timer setting on the overhead liquid reflux divider. The boil-up rate was about 0.5 liter per hour.

The fractions were analyzed by gas chromatography using a Perkin Elmer 154-D Vapor Fractometer with a packed column containing 2 meters of 7,8-benzoquinoline on Chromosorb P. Operating temperature was 100° C. using helium as a carrier at about 20 p.s.i.g. inlet pressure. Using a thermal conductivity detector, this technique will completely resolve the individual C_8 aromatic isomers and tetrachloroethane and will detect 0.01 wt. % of a given isomer.

The xylenes and tetrachloroethane were the best grades obtainable from Matheson, Coleman, and Bell and were used without further purification. The *o*-xylene was 99.3% pure, the *m*-xylene 99.5% pure, and the tetrachloroethane was 95.5% pure as measured by the G.C. analysis.

Due to the design of the overhead condenser on the distillation column, the reported overhead temperatures are slightly low. It is estimated that this error is on the order of 1.5° C. but varies somewhat with boilup rate.

RESULTS

The distillation of an equimolar C_8 aromatic mixture is shown in Figure 1 where the composition of the distillation cuts is plotted *vs.* the mid-volume percent distilled. The mid-volume percent distilled is the amount distilled at the mid-point of each cut. These curves show a steady increase in tetrachloroethane content of the overhead fractions until about 70% of the charge has been distilled and then a rapid decrease as the *o*-xylene content sharply increases. The nature of this distillation during the last 20% off led to the suspicion of a maximum boiling *o*-xylene azeotrope and further binary distillations were made to characterize it.

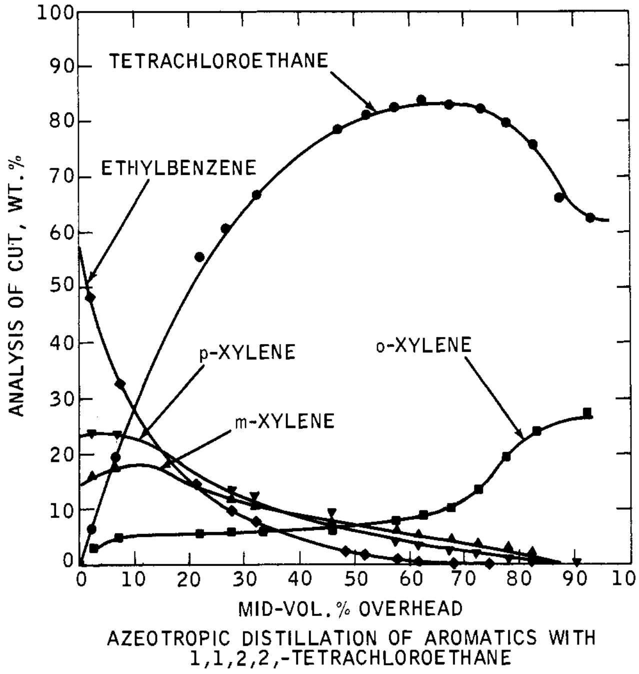

Figure 1. Azeotropic distillation of aromatics with 1,1,2,2-tetrachloroethane

Two binary distillations were run starting with 35.4 wt. % *o*-xylene in 1,1,2,2,-tetrachloroethane for Distillation No. 1 and 24.7 wt. % *o*-xylene in the tetrachloroethane for Distillation No. 2. The composition of the overhead cuts is given in Table I and plotted in Figure 2.

Both of these distillations gave the same bottoms composition although starting with feed compositions above and below this constant bottoms composition. This is definite proof that a maximum boiling azeotrope of 29.8 wt. % *o*-xylene in 1,1,2,2-tetrachloroethane is formed. The uncorrected boiling point of this azeotrope is about 146° C. leading to a corrected value of about 147.5 ± 0.5° C. at atmospheric pressure.

The occurrence of a maximum boiling azeotrope between 1,1,2,2-tetrachloroethane and *o*-xylene is very probably due to hydrogen bonding between the hydrogens of the hydrocarbon and the chlorine atoms in the tetrachloroethane. Numerous other cases of maximum boiling azeotropes of halogenated hydrocarbons are known (*1*).

Two distillations were also run on mixtures of *m*-xylene and 1,1,2,2-tetrachloroethane to look for a maximum boiling azeotrope of these materials. These are plotted in Figure 3 and the data are given in Table II. The first distillation started with a feed composition of 34.7 wt. % *m*-xylene and showed no signs of an azeotrope down to a bottoms composition of 5.7 wt. % *m*-xylene. The second distillation started

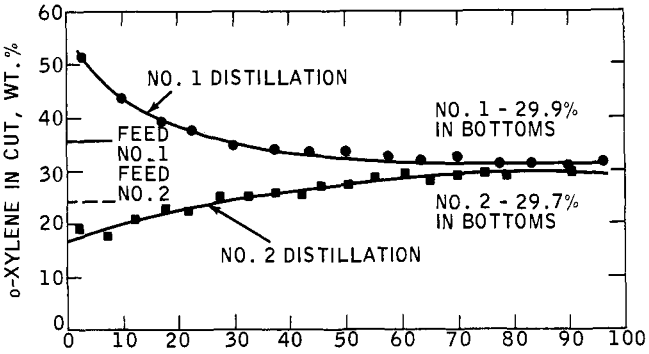

Figure 2. Distillation of o-xylene–1,1,2,2-tetrachloroethane mixtures

Table I. Azeotropic Distillation of o-Xylene with 1,1,2,2-Tetrachloroethane

Charge: 450 ml. of 64.6 Wt. % 1,1,2,2-tetrachloroethane-35.4 Wt. % *o*-xylene mixture.
Reflux Ratio = 5:1.
Column: 1-inch diameter × 3 ft. packed section using 3/16-inch Cannon protruded packing. Equivalent to 20 theoretical plates.

Cut No.	Vol. % Off.	Mid-Vol. % Off.	Uncorrected Temp., ° C. Overhead	Uncorrected Temp., ° C. Still pot	Product Analysis, Wt. % *o*-Xylene
1	6.7	3.3	145	148	51.1
2	13.3	10.0	145.5	148	42.2
3	20.0	16.6	145.5	148	39.1
4	26.7	23.3	145.5	148	36.5
5	33.3	30.0	145.5	148	35.1
6	40.0	36.6	145.5	148	34.1
7	46.7	43.3	145.5	148	33.5
8	53.3	50.0	145.5	148	33.2
9	60.0	56.6	145.5	148	32.3
10	66.7	63.3	145.5	148	31.5
11	73.3	70.0	145.5	148	31.5
12	80.0	76.6	145.5	148	30.3
13	86.7	83.3	145.5	154	29.7
14	93.3	90.0	145.5	199	29.5
Bottoms	100.0	96.6	. . .	. . .	29.9

Recharged still with 450 ml. of 75.3 Wt. % 1,1,2,2-tetrachloroethane-24.7 Wt. % *o*-xylene and distilled at 5:1 reflux ratio taking 22 ml. cuts.

1	4.8	2.4	. . .	. . .	19.3
2	9.6	7.2	. . .	. . .	17.9
3	14.5	12.0	146	147	20.9
4	19.3	16.9	146	147	22.0
5	24.1	21.7	146	147	22.1
6	28.9	26.5	146	147	23.6
7	33.8	31.3	146	147	23.8
8	38.6	36.2	146	147	24.1
9	43.4	41.0	146	147	24.0
10	48.2	45.8	146.2	147	25.3
11	53.0	50.6	146.2	147	26.1
12	57.9	55.4	146.2	147	27.1
13	62.6	60.3	146.2	147	27.8
14	67.5	65.0	146.2	147	27.3
15	72.3	69.9	146.2	148	28.3
16	77.1	76.7	146.2	150	28.7
17	82.0	79.5	146.5	217	28.5
Bottoms	100.0	91.0	. . .	. . .	29.7

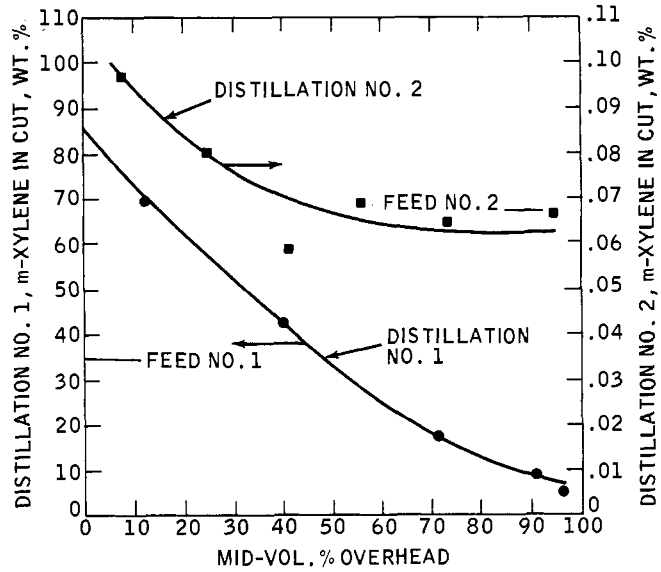

Figure 3. Distillation of *m*-xylene–1,1,2,2-tetrachloroethane mixtures

Table II. Azeotropic Distillation of *m*-Xylene with 1,1,2,2-Tetrachloroethane

Charge: 850 ml. of mixture of 65.3 Wt. % 1,1,2,2-tetrachloroethane and 34.7 Wt. % *m*-xylene.
Reflux Ratio = 5:1
Column: 1-inch diameter × 3 ft. packed section using 3/16-inch Cannon protruded packing. Equivalent to 20 theoretical plates.

Cut No.	Vol. of Cut, Ml.	Vol. % Off.	Mid-Vol. % off.	Uncorrected Temp., ° C. Overhead	Uncorrected Temp., ° C. Still Pot	Product Analysis, Wt. % *m*-Xylene
1	216	25.4	12.7	133.7	149	69.6
2	262	56.2	40.8	143.0	149	42.4
3	253	86.1	71.2	143.0	150	16.9
4	66	94.8	90.5	143.0	. . .	9.2
[a]	53	100.0	97.4	. . .	. . .	5.7

Recharged with 1246 ml. of 0.066 Wt. % *m*-xylene in 1,1,2,2-tetrachloroethane and distilled at 5:1 Reflux Ratio.

1	207	16.6	8.5	127	149	0.096
2	205	32.9	24.8	133	149	0.080
3	200	49.0	40.9	140	149	0.059
4	200	65.0	57.0	140	150	0.069
5	203	81.4	73.2	140	150	0.064
6	137	92.2	86.8	140	153	0.056
[a]	95	100.0	96.1	. . .	153	0.066
			Average, column seven, last five values:			0.063

[a] Bottoms.

with a feed composition of 0.066 wt. % *m*-xylene in 1,1,2,2-tetrachloroethane. About 50% of the overhead product from 50% to 100% off, including the bottoms, had a composition averaging 0.063 wt. % *m*-xylene with an average deviation from this value of 0.004 wt. %. Although an azeotrope should be approached from both sides to confirm its presence, it is felt that this constant composition probably represents a maximum boiling azeotrope of *m*-xylene and 1,1,2,2-tetrachloroethane containing about 0.063 wt. % *m*-xylene.

There is also a possibility that the *m*-xylene is really azeotroping with some impurity in the tetrachloroethane. However, such impurities are present only in trace quantities in Fractions 3 to 6 of Table II and therefore such an azeotrope would have to contain predominantly *m*-xylene and should boil close to *m*-xylene. It would not be expected to concentrate in the back end of the distillation. Thus, it is felt that the *m*-xylene-1,1,2,2-tetrachloroethane azeotrope is real.

ACKNOWLEDGMENT

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Zirconium Carbide: Heat Capacity and Thermodynamic Properties from 5 to 350° K.

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The heat capacity of a characterized, zone-melted sample of ZrC was measured by adiabatic calorimetry from 5° to 350° K. and found to be of normal sigmoid shape without transitions or thermal anomalies. At 298.15° K. the measured heat capacity at constant pressure (C_p), the practical entropy ($S°$), the enthalpy function ($[H° - H°_0]/T$), and the Gibbs function ($-[G° - H°_0]/T$) are 9.06, 7.96, 4.70, and 3.26 cal. (g.f.m. ° K.)$^{-1}$. Values of the heat capacity and entropy, adjusted to pure ZrC on the basis of the impurity content obtained by chemical analysis, are 9.13 and 7.90 cal. (g.f.m. ° K.)$^{-1}$.

PREVIOUS studies (3, 6-9, 11, 12) have provided values for thermodynamic properties of zirconium carbide (ZrC). The enthalpy of combustion of zirconium carbide was measured by Mah and Boyle (9) who derived the value −44.0 ± 1.5 kcal. for the enthalpy of formation at 298.15° K. Krikorian reviewed the available data for the carbides and estimated heat capacity and entropy by assuming that the difference between the heat capacities of zirconium carbide and zirconium nitride was equal to that between titanium carbide and titanium nitride. Using the entropies of these compounds recommended by Kelley and King (5) the entropy of zirconium carbide was estimated at 7.8 ± 0.5 cal. (g.f.m. ° K.)$^{-1}$. The heat capacity estimate was made by using the data of Coughlin and King (1) on zirconium nitride and the data of Naylor (10) on titanium carbide and titanium nitride. Kelley and King (5) recently estimated the entropy at 298.15° K. as 9.3 ± 0.3 cal. (g.f.m. ° K.)$^{-1}$. Experimental enthalpy increments over the range of 470° to 1174° K. referred to 298° K. have been obtained by Margrave [reported by McClaine (8)] and accord well with the present measurements. The other investigations cited involve studies on the vaporization and equilibrium properties of systems involving zirconium carbide at high temperatures. The present investigations were made to provide a definitive value for the entropy and low temperature chemical thermodynamic properties.

EXPERIMENTAL

Cryostat and Calorimeter. Measurements were made in the Mark II adiabatic vacuum cryostat, which provided an instrument of greater efficiency, mechanical rigidity, and operating convenience than a prototype previously described (13). A heat exchanger in the metal cryostat utilizes the enthalpy of the effluent helium gas to furnish a thermal dam for the conduction of heat by the bundle of electrical leads and thus minimize vaporization of the liquid helium from the lowest temperature reservoir. The calorimeter itself is surrounded by a cylindrical adiabatic shield; three portions of the shield are individually controlled by separate channels of automatic regulation which provide a.c. power to the several separate heaters. Copper-Constantan thermocouples monitor the temperature difference between calorimeter and shield and between shield and the ring used to temper the gradient in the bundle of leads. Three separate channels of recording electronic circuitry having proportional, rate, and reset control actions regulate temperature differences to within a millidegree over the range 50° to 350° K. Energy exchange between the calorimeter and the surroundings is so reduced that it is negligible compared with other sources of error. The adiabatic method of operation has been described (13).

The copper calorimeter of laboratory designation W-31, a gold-plated vessel with a capacity of 50 cc., has an offset thermometer well which projects through the bottom of the calorimeter for approximately a centimeter, but no thermal conduction vanes. The heat capacity of the empty calorimeter was determined in a separate series of measurements in which identical amounts of indium-tin solder for sealing the calorimeter and Apiezon-T grease for thermal contact with the heater-thermometer-calorimeter assembly were used. At the lowest temperatures the heat capacity of the sample represented 30% of the total. This increased to 50% at 55° K., to 70% at 170° K., and to 76% by 350° K. and hence was a favorable fraction of the total over most of the range. The mass of the calorimetric sample was 125.948 grams (in vacuo). Buoyancy corrections were made by using a density of 6.73 grams cc.$^{-1}$ for zirconium carbide. A pressure of 13.6 cm. of helium at 300° K. was used to facilitate thermal conduction in the sample space.

Temperatures were determined with a capsule-type, strain-free, platinum-resistance thermometer (laboratory designation A-5) contained within an entrant well in the calorimeter. Temperatures are considered to accord with