Azeotropic Data on Chlorinated Hydrocarbons

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Conflicting data have appeared in the literature on the three azeotropic systems: carbon tetrachloride–1,2-dichloroethane, 1,2-dichloroethane–trichloroethylene, and 1,1,2-trichloroethane–perchloroethylene. Therefore a study of the azeotropic composition and boiling points of these systems was undertaken.

APPARATUS

The distillations were carried out in a standard 42-plate Todd Scientific Co. laboratory scale packed column.

The azeotropic boiling points were measured using an ASTM distillation of the azeotropes. Refractive indices were measured at 25 °C. on an Abbe refractometer.

PREPARATION OF REAGENTS

The chemicals purchased for this study were:

Name	Source	Grade	Purity, Wt. %
Carbon tetrachloride	Baker	C. P.	Min. 99
1,2-Dichloroethane	Olin Mathieson		Min. 99
Trichloroethylene	Niagara Alkali	Unstabilized[a] and noninhibited	Min. 99
Perchloroethylene	Diamond Alkali	Unstabilized[a] and noninhibited	Min. 99
1,1,2-Trichloroethane	Union Carbide	Technical	90–95

[a] Specially purchased.

The samples used for the binary refractive index-composition curves (with the exception of carbon tetrachloride) were purified by fractionation. A heart cut of the material was used.

The carbon tetrachloride, trichloroethylene, and perchloroethylene were considered pure enough to use directly in the azeotropic study. The 1,2-dichloroethane and 1,1,2-trichloroethane were purified by distillation.

All analyses were made by refractive index. Table I is a summary of the refractive index data on the binary systems.

EXPERIMENTAL PROCEDURE

Carbon Tetrachloride-1,2-Dichloroethane Azeotrope. A 1030-ml. charge of 79 weight % carbon tetrachloride–21% 1,2-dichloroethane was fractionated at about a 5 to 1 reflux ratio on the 42-plate column. A total of 100 ml. of material was taken overhead with a constant boiling point of 75.5 °C. and constant n_D^{25} of 1.4518, corresponding to 80 ± 1 % of carbon tetrachloride. Five hundred milliliters were then removed with no reflux; 100 ml. were taken overhead at a 5 to 1 reflux ratio and at the same temperature and refractive index. As the overhead composition did not change within the limit of error of the analytical method during the course of the fractionation, it can be concluded that 80 ± 1 weight % of carbon tetrachloride-20 ∓ 1 % of 1,2-dichloroethane is the azeotropic composition. This value compares favorably with Young and Nelson's value of 78.4 weight % of carbon tetrachloride–21.6% of 1,2-dichloroethane (*4*).

Table I. Refractive Indices of the Binary Systems

Composition, Wt. % First Component	n_D^{25}
A. Carbon Tetrachloride–1,2-Dichloroethane	
0	1.4416
19.6	1.4437
38.7	1.4457
60.1	1.4484
80.2	1.4518
100.0	1.4568
B. 1,2-Dichloroethane–Trichloroethylene	
0	1.4743
16.3	1.4670
36.6	1.4598
56.0	1.4537
82.4	1.4461
100.0	1.4416
C. 1,1,2-Trichloroethane–Perchloroethylene	
0	1.5024
23.5	1.4916
43.4	1.4837
61.5	1.4783
80.7	1.4728
100.0	1.4684

Table II. Rectification of 1,2-Dichloroethane–Trichloroethylene Mixtures

(Ultimate separations at about 200 to 1 reflux ratio)

Run No.	1,2-Dichloroethane in Bottoms[a], Wt. %	n_D^{25} Overhead	1,2-Dichloroethane in Overhead[b], Wt. %	B. P., °C.	Notes
1	48	1.4528	59	82	Crosses Reid's azeotrope
2	92	1.4496	70	82	Crosses Lecat's azeotrope
3	70	1.4519	62	81	
4	61	1.4522	61	82	True azeotrope overhead

[a] Calculated from material balance.
[b] From refractive index–composition curve.

The corrected boiling point of the azeotrope was determined by distilling a mixture of azeotropic composition in a simple still, measuring the overhead temperature, and correcting to 760 mm. of pressure. The corrected value of 75.5 °C. verifies that of Young and Nelson, which is 75.3 °C.

1,2-Dichloroethane-Trichloroethylene. Four distillations were made (Table II, runs 1 to 4). Run 1 consisted of fractionating a 370-ml. batch of 50 weight % of 1,2-dichloroethane. A total of 64 ml. was taken overhead alternating between 2 to 1 and about 200 to 1 reflux ratio until a constant overhead composition was obtained. The bottoms composition in equilibrium with this overhead material was calculated from the overhead composition plus charge composition. Run 2 consisted of fractionating a 140-ml. batch of 88 weight % of 1,2-dichloroethane. A total of 50 ml. was

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Table III. Rectification of 1,1,2-Trichloroethane–Perchloroethylene Mixtures

(Ultimate separations at about 200 to 1 reflux ratio)

Run No.	1,1,2-Tri chloroethane in Bottoms^a, Wt. %	n_D^{25} Overhead	1,1,2-Trichloroethane in Overhead^b, Wt. %	B. P., °C.	Notes
1	27	1.4755	71	112	Crosses Horsley's azeotrope
2	91	1.4737	77	112	
3	76	1.4747	74	112	True azeotrope overhead
4	73	1.4747	74	112	True azeotrope overhead

^{a}Calculated from material balance.
^{b}From refractive index–composition curve.

taken overhead alternating between 2 to 1 and about 200 to 1 reflux ratio until a constant overhead composition was obtained. Run 3 utilized a 620-ml. charge of 69 weight % of 1,2-dichloroethane which, upon removal of 69 ml. of overhead in the same manner as before, resulted in a bottoms composition of 70 weight % of 1,2-dichloroethane rectified to an overhead composition of 62%. Runs 1 and 3 bracket the azeotropic "pinch" between 59 and 62 weight % of 1,2-dichloroethane. Therefore run 4 was made with 155 ml. of 61 weight % of 1,2-dichloroethane. Removal of 88 ml. of overhead yielded overhead material of precisely the same composition as the bottoms (alternating between 2 to 1 and 200 to 1 reflux ratio). The azeotropic composition is, therefore, 61 weight % of 1,2-dichloroethane–39 weight % of trichloroethylene. This value can be considered to have the same ±1% degree of precision as the previous azeotropic composition. The corrected boiling point is 82.2° ± 0.2°C., determined as before.

1,1,2-Trichloroethane–Perchloroethylene. The same procedure was used for this azeotrope as for the two previous ones. Four distillations were carried out (Table III). In run 1 rectification of bottoms material of 27 weight % of 1,1,2-trichloroethane to an overhead composition of 71% eliminates the possibility of an azeotrope in that range. Run 2 consisted of boiling 88 weight % of 1,1,2-trichloroethane in the same manner. The final separation values were 91 weight % of 1,1,2-trichloroethane in the bottoms and 77% overhead. Runs 1 and 2 bracket the azeotropic pinch between 71 and 77 weight % of 1,1,2-trichloroethane. Runs 3 and 4 establish the actual azeotropic composition. In Run 3 76 weight % of 1,1,2-trichloroethane mixture was rectified to an overhead composition of 74%. In run 4 a 73% mixture was rectified to 74%. The azeotropic composition is, therefore, 74 ±1 weight % of 1,1,2-trichloroethane–26 ± 1 weight % of perchloroethylene. The corrected boiling point is 112.9° ±0.2°C., determined as before.

CONCLUSIONS

The boiling points and compositions of the three binary, minimum-boiling, homogeneous azeotropes investigated are:

	Composition, Weight % First Component		Azeotropic B.P., °C.	
System	This work	Lit.	This work	Lit.
Carbon tetrachloride–1,2-dichloroethane	80 ± 1	78.4(4)	75.5 ± 0.2	75.3(4)
1,2-Dichloroethane–trichloroethylene	61 ± 1	82.0(2) 56.5(3)	82.2 ± 0.2	82.6(2) 82.1(3)
1,1,2-Trichloroethane–perchloroethylene	74 ± 1	43.0(1)	112.9 ± 0.2	112.0(1)

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Correlation of Vapor-Liquid Equilibrium Data for Acetone-Water System

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The system acetone-water was studied by several workers and vapor-liquid equilibrium data covering a range of isobaric and isothermal conditions are available. The present work includes all data at 760-mm. pressure and below, and isothermal data below 100°C.

VAPOR PRESSURE DATA OF PURE COMPONENTS

Acetone. To correlate activity coefficients, the vapor pressure of acetone is required. All available data (*1,8,11,28–31*) were collected and expressed in the form of an Antoine equation,

$$\log P = 6.962 - 1120.32/(218.38 + t) \qquad (1)$$

P is in millimeters of mercury. The atmospheric boiling point determined by using Equation 1 agrees well with the value given by U.S. Industrial Chemicals (*35*). Timmermans (*33*) lists values ranging from 56.1° to 56.6°C.

Water. Vapor pressure data for water are taken from Perry (*24*).

CORRELATION OF ISOTHERMAL EQUILIBRIUM DATA

All available data (*10,13,14,16,18*) at and below 100°C. were used.

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