Isobaric Vapor–Liquid Equilibria of the *p*-Xylene–1,1,1-Trichloroethane System

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Isobaric vapor–liquid equilibria of the *p*-xylene–1,1,1-trichloroethane system were measured at 665-mmHg pressure. Activity coefficients were evaluated and correlated. Vapor pressures of 1,1,1-trichloroethane in the range of 600–1750 mmHg are also reported.

This second paper on the vapor–liquid equilibria of *p*-xylene–chloroethane systems presents data for the *p*-xylene–1,1,1-trichloroethane system. Previous studies have presented data for benzene and toluene with 1,1,1-trichloroethane (*1*, *2*).

Experimental Section

Vapor–liquid equilibria were established by using a modified Brown still. The description and the operation of the apparatus have been reported (*3*). The chemicals were purified as described earlier (*2*, *3*) and the measured physical properties are tabulated in Table I. The purity of the chemicals is assessed to be better than 99.95 mol%. The compositions of the condensed vapor and liquid samples were analyzed by using a Pulfrich precision refractometer and the measurements were carried out at 303.15 ± 0.05 K. The refractive index–composition data presented in Table II fit the equation

$$n^{30}_{D} = 1.431785 + 0.0703757X_1 - 0.01228X_1^2 + 0.000595479X_1^3 \quad (1)$$

with an average absolute deviation of 0.005% and a maximum deviation of 0.014%.

Results

The experimentally determined values of T, X, Y, together with the calculated values of activity coefficients γ_1, γ_2 and the gas-phase imperfections Z_1, Z_2 are tabulated in Table III. The values of Z_1, Z_2, γ_1, and γ_2 were evaluated as described earlier (*3*). Experimental T, X, Y data are shown in Figure 1. The vapor pressure data taken in the present investigation are in better agreement with the data of Ambrose, Sparke, and Townsend (*4*) compared to the data reported earlier by Sundaram and Viswanath (*2*). The experimentally determined values of vapor pressure are listed in Table IV. The data fit the equation

$$\log (P_2^0/P_c) = \sum_{j=1}^{5} a_j\{(T_c/T) - 1.0\}^{0.5j} \quad (2)$$

with the coefficients $a_1 = 295.5068$, $a_2 = -1616.7341$, $a_3 = 3288.2325$, $a_4 = -2980.8015$, and $a_5 = 1011.6958$. For a total of 56 data points, eq 2 gave an average absolute deviation of 0.21% and a maximum deviation of 0.5%. The present data along with the literature data are shown graphically in Figure 2. The second virial coefficient data required to calculate the vapor-phase imperfections were taken from the data reported by Dymond and Smith (*5*) and Cox and Andon (*6*). The interaction virial coefficients were evaluated as described earlier (*3*). The force constants used for the pure substances were as follows: *p*-xylene, $\epsilon/k = 645.0$ K, $\sigma = 6.810$ Å; 1,1,1-trichloroethane $\epsilon/k = 518.8$ K, $\sigma = 6.123$ Å. These data were used to calculate vapor-phase imperfections and activity coefficients by using the relations

$$\log \gamma_1 = \log (Y_1P/X_1P_1^0) + 0.4342 \ln Z_1 \quad (3)$$

$$\log \gamma_2 = \log (Y_2P/X_2P_2^0) + 0.4342 \ln Z_2 \quad (4)$$

where

$$Z_1 = \exp\{[(P - P_1^0)(B_{11} - V_1^L) + PY_2^2\delta_{12}]/RT\} \quad (5)$$

$$Z_2 = \exp\{[(P - P_2^0)(B_{22} - V_2^L) + PY_1^2\delta_{12}]/RT\} \quad (6)$$

Correlation of Activity Coefficients

The activity coefficients calculated from eq 3 and 4 were correlated by using Wilson and Redlich–Kister equations. The parameters Λ_{12} and Λ_{21} in the Wilson equations

$$\ln \gamma_1 = -\ln A + X_2[(\Lambda_{12}/A) - (\Lambda_{21}/B)] \quad (7)$$

$$\ln \gamma_2 = -\ln B - X_1[(\Lambda_{12}/A) - (\Lambda_{21}/B)] \quad (8)$$

where

$$A = X_1 + \Lambda_{12}X_2 \qquad B = X_2 + \Lambda_{21}X_1$$

were evaluated by using the least-squares method minimizing the error between experimental and Wilson γ values. The same technique was followed in fitting the activity coefficients to the Redlich–Kister equations

$$\ln \gamma_1 = X_2^2\{A_1 + A_2(3X_1 - X_2) + A_3(X_1 - X_2)(5X_1 - X_2)\} \quad (9)$$

$$\ln \gamma_2 = X_1^2\{A_1 + A_2(X_1 - 3X_2) + A_3(X_1 - X_2)(X_1 - 5X_2)\} \quad (10)$$

The constants for these equations and a comparison of the two correlations are summarized in Table V.

Thermodynamic Consistency

The experimental data have been tested for thermodynamic consistency by using Herington's method and the rigorous Gibbs–Duhem relation by evaluating the integrals

$$I_1 = \int_0^1 \log (\gamma_1/\gamma_2)\, dX_1 \quad (11)$$

$$I_2 = \int_0^1 [-H^E/(2.303RT^2)](dT/dX_1)\, dX_1 \quad (12)$$

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Table I. Physical Properties of Substances at 303.15 ± 0.05 K

substance	refractive index[a] exptl	refractive index[a] lit.	density,[a] g cm^{-3} exptl	density,[a] g cm^{-3} lit.	bp, K exptl	bp, K lit.
p-xylene	1.4905	1.4904 (*8*)	0.8527	0.8524 (*8*)	286.35	286.40 (*8*)[b]
1,1,1-trichloroethane	1.4317	1.4320 (*8*)	1.3211	1.3209 (*9*)	347.20	347.25 (*10*)

[a] Refractive index and density measured to ±0.0001. [b] Freezing point.

Table II. Refractive Index-Composition for the System *p*-Xylene-1,1,1-Trichloroethane at 303.15 ± 0.05 K

X_1[a]	$n^{30}{}_D$[b]	X_1[a]	$n^{30}{}_D$[b]
0.0	1.4317	0.5477	1.4669
0.0518	1.4354	0.6031	1.4699
0.0969	1.4385	0.6576	1.4730
0.1566	1.4426	0.7042	1.4755
0.1931	1.4451	0.7624	1.4785
0.2627	1.4493	0.8060	1.4808
0.2991	1.4517	0.8486	1.4830
0.3371	1.4540	0.9035	1.4858
0.3956	1.4578	0.9530	1.4882
0.4447	1.4605	1.0000	1.4905
0.4976	1.4639		

[a] Mole fraction of *p*-xylene. [b] Refractive index.

Table III. Vapor-Liquid Equilibrium Data for the *p*-Xylene-1,1,1-Trichloroethane System at 685 mmHg

T, K	X_1	Y_1	γ_1	γ_2	Z_1	Z_2
345.30	0.0490	0.0060	0.9136	1.0019	0.9402	1.0017
348.05	0.1370	0.0190	0.9311	1.0034	0.9423	1.0053
352.85	0.2670	0.0460	0.9625	0.9992	0.9460	1.0110
356.75	0.3490	0.0700	0.9695	0.9797	0.9490	1.0170
358.35	0.3740	0.0790	0.9633	0.9639	0.9503	1.0200
361.55	0.4500	0.1100	0.9939	0.9761	0.9528	1.0240
365.05	0.5100	0.1400	0.9875	0.9616	0.9557	1.0300
369.15	0.5800	0.1850	0.9978	0.9601	0.9592	1.0360
372.85	0.6350	0.2280	0.9933	0.9530	0.9625	1.0430
376.75	0.6900	0.2820	0.9966	0.9503	0.9661	1.0503
380.30	0.7350	0.3350	0.9937	0.9467	0.9696	1.0569
386.25	0.7980	0.4300	0.9794	0.9303	0.9755	1.0683
391.15	0.8480	0.5250	0.9739	0.9242	0.9807	1.0785
394.90	0.8950	0.6350	1.0022	0.9504	0.9848	1.0865
400.75	0.9420	0.7760	0.9889	0.9349	0.9914	1.1000

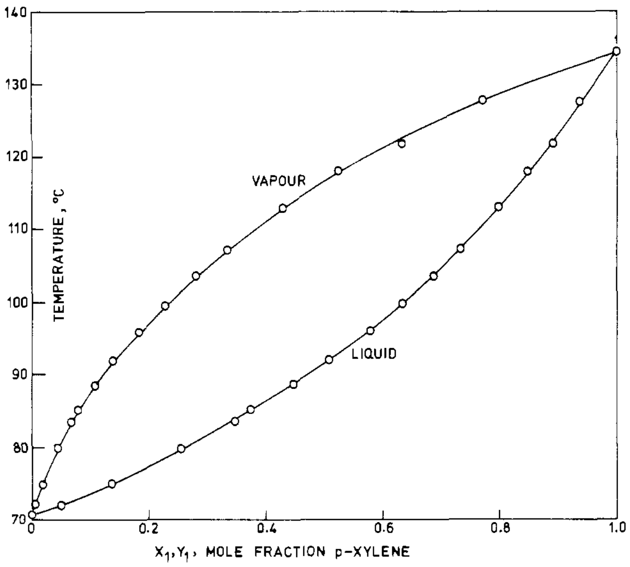

Figure 1. *T-X-Y* of *p*-xylene-1,1,1-trichloroethane system.

I_1 was evaluated from a graph of log (γ_1/γ_2) and X_1. To evaluate I_2, we fitted the bubble temperature-composition data to the relation

$$T = \sum_{i=1}^{4} B_i X^{i-1} \tag{13}$$

Table IV. Experimental Vapor Pressures of 1,1,1-Trichloroethane

T, K	$P_2{}^0{}_{\text{exptl}}$, mmHg	$\delta P_2{}^0$[a]	*T*, K	$P_2{}^0{}_{\text{exptl}}$, mmHg	$\delta P_2{}^0$[a]
340.70	618.0	0.24	359.25	1095.5	0.43
341.40	632.0	0.22	359.70	1103.5	−0.12
342.00	642.7	−0.03	360.85	1138.5	−0.27
342.55	655.1	0.10	362.05	1178.5	−0.21
343.00	663.1	−0.13	362.45	1194.5	0.01
343.95	684.0	−0.07	362.75	1207.5	0.26
344.00	686.0	0.05	363.25	1221.5	0.02
345.35	717.0	0.17	364.45	1263.5	0.07
346.15	730.5	−0.50	365.45	1303.5	0.43
346.25	735.9	−0.08	366.25	1331.5	0.36
346.50	743.2	0.12	366.45	1337.5	0.26
347.20	760.0	0.14	367.75	1382.0	0.01
348.15	782.5	0.08	368.55	1408.5	−0.26
349.50	817.5	0.26	368.65	1414.0	−0.14
349.55	818.8	0.26	369.20	1443.5	0.44
349.65	819.0	−0.02	369.95	1463.0	−0.23
350.75	850.5	0.36	370.85	1501.5	−0.04
351.75	872.5	−0.14	371.75	1534.5	−0.27
353.20	910.0	−0.32	371.95	1552.0	0.32
353.70	924.5	−0.25	372.95	1586.5	−0.14
354.45	951.8	0.42	373.05	1592.5	0.10
354.70	956.5	0.16	373.65	1621.0	0.15
355.10	963.9	−0.25	374.25	1650.0	0.33
355.45	976.5	0.01	374.40	1656.5	0.32
356.95	1021.2	0.07	374.45	1657.0	0.22
357.90	1048.8	−0.02	375.35	1689.0	−0.25
358.35	1065.5	0.25	375.95	1723.5	0.18
358.45	1069.5	0.33	376.75	1752.0	−0.30

[a] $\delta P_2{}^0 = 100\{(P_2{}^0{}_{\text{exptl}} - P_2{}^0{}_{\text{calcd}})/P_2{}^0{}_{\text{exptl}}\}$. $P_2{}^0{}_{\text{calcd}}$ from eq 2.

Table V. Constants for Eq 7-10 and Deviation in Activity Coefficients

correlation	constants	$\delta\gamma_1$[a]
Wilson	$\Lambda_{12} = 1.1020$ $\Lambda_{21} = 0.9820$	1.00
Redlich-Kister	$A_1 = -0.06790$ $A_2 = -0.12380$ $A_3 = -0.13664$	2.49

[a] $\delta\gamma_1 = \{\Sigma_{i=1}^{n} |[(\gamma_{1,\text{exptl}} - \gamma_{1,\text{calcd}})/\gamma_{1,\text{exptl}}]|\}(100/n)$ where *n* is the number of experimental points.

Equation 13 fitted the *T*-*X* data with an average absolute deviation of 0.06% and a maximum deviation of 0.14% with $B_1 = 343.50$, $B_2 = 33.83$, $B_3 = 1.60$, and $B_4 = 28.47$, the constants being evaluated by using the least-squares technique. Using eq 13 to get the necessary derivative, we evaluated I_2 numerically with Simpson's rule. The enthalpies of mixing measured at 308.15 K (*7*) were used in evaluating I_2. The values of I_1 and I_2 were 0.002 04 and −0.001 95 ($I_1 + I_2 = 0.00009$), respectively, thus indicating the consistency of the data and the importance of the second integral I_2 in checking the consistency of the data. The vapor-liquid equilibria presented in Table III cover a range of temperature from 340 to 400 K. However, the excess enthalpies measured at 308.15 K were used to evaluate the integral I_2. This is justified as excess enthalpy values are small, the maximum values being 100 J mol^{-1} at 298.15 K and 170 J mol^{-1} at 308.15 K occurring at a mole fraction of *p*-xylene around 0.45. Therefore, excess enthalpy values available at the highest temperature were used

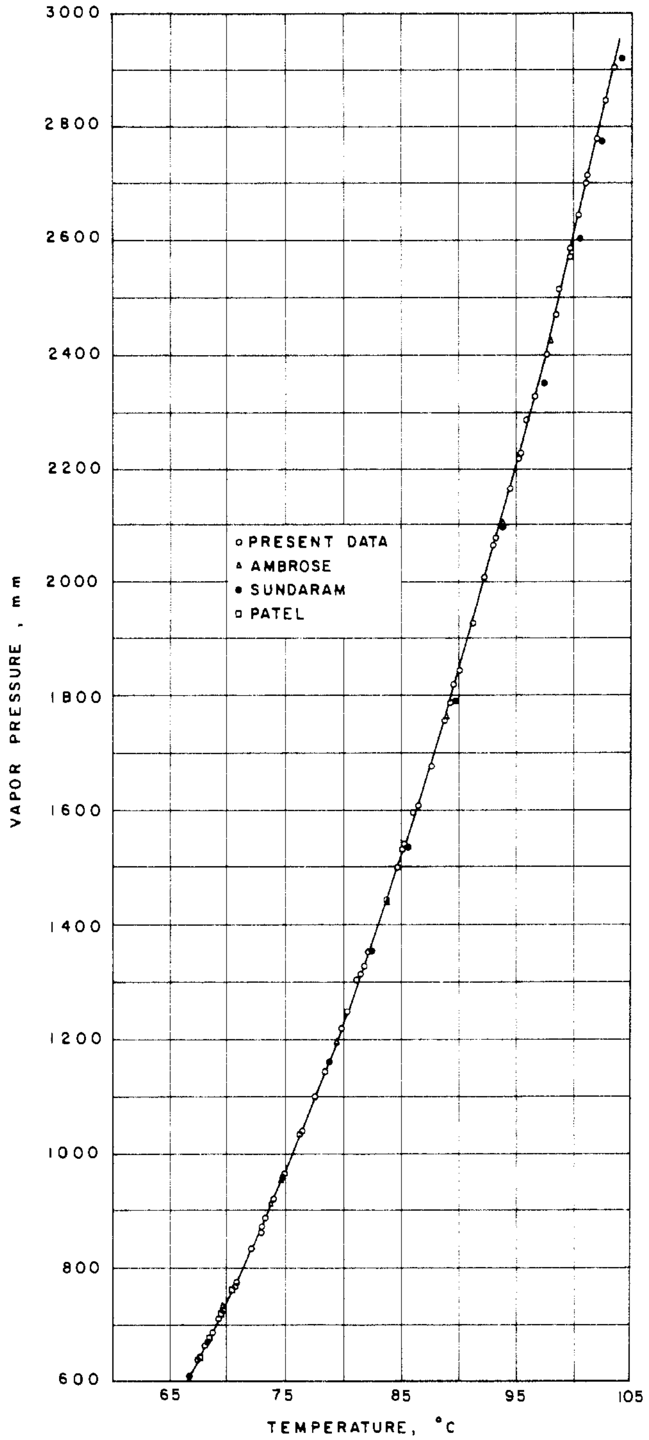

Figure 2. Vapor pressure of 1,1,1-trichloroethane.

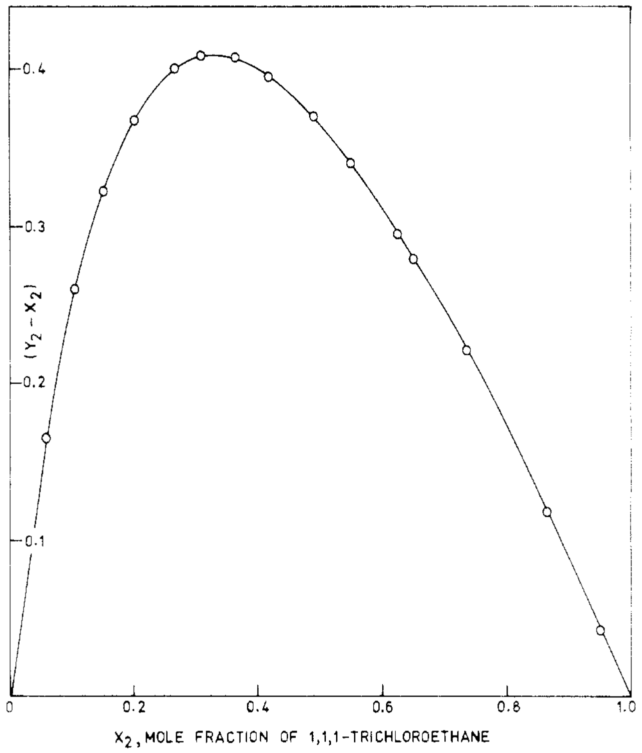

Figure 3. $Y_2 - X_2$ vs. X_2 for *p*-xylene–1,1,1-trichloroethane system.

ignoring the temperature dependence. Even if the excess enthalpies are of the order of 1–2 kJ mol^{-1} as exemplified by the *p*-xylene–1,1,2,2-tetrachloroethane (*11*), temperature independence can be assumed for the area test without sacrificing a great deal of accuracy. However, when one calculates other properties like enthalpies of vaporization using excess enthalpies and heat capacities, care should be exercised. It is essential to use the excess enthalpy value at the particular temperature. In many cases a linear extrapolation will suffice. The application of the Herington test also showed that the data are consistent with $D = 10.37$ and $J = 27.80$, giving a value of $D - J < 10$. An error analysis performed on γ_1 and γ_2 revealed the maximum errors in γ_1 and γ_2 to be 1.99% and 0.24%, respectively. The values of $Y_2 - X_2$ shown in Figure 3 reveal that there are no random experimental errors. In evaluating the maximum errors in γ_1 and γ_2, we take the accuracy in pressure, composition, and temperature to be ±0.1 mmHg, ±0.0001, and ±0.05 K although the accuracies were better than these figures. When one takes into consideration the purity of the chemicals, accuracy of measurements, and the agreement of the data with the available data, the data presented in this paper can be considered accurate and reliable.

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Literature Cited

(1) Patel, H. R.; Sundaram, S.; Viswanath, D. S. *J. Chem. Eng. Data* **1979**, *24*, 40.
(2) Sundaram, S.; Viswanath, D. S. *Can. J. Chem. Eng.* **1979**, *57*, 233.
(3) Rao, M. V.; Viswanath, D. S. *J. Chem. Eng. Data* **1982**, *27*, 41.
(4) Ambrose, D.; Sparke, C. H. S.; Townsend, R. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 839.
(5) Dymond, J. H.; Smith, E. B. "The Virial Coefficients of Gases"; Clarendon Press: Oxford, 1969; pp 50, 147.
(6) Cox, J. D.; Andon, R. J. L. *Trans. Faraday Soc.* **1958**, *54*, 1622.
(7) Rao, M. V. Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1980.
(8) (a) Driesbach, R. R. "Physical Properties of Chemical Compounds"; American Chemical Society: Washington, DC, 1955; Vol. I, p 16. (b) *Ibid*. 1959; Vol. II, p 204.
(9) Timmermans, J. "Physico-chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1965; p 242.
(10) Reddick, J. A.; Bunger, W. B. "Techniques of Chemistry", 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II, p 357.
(11) Rao, M. V.; Viswanath, D. S. *J. Chem. Eng. Data*, following paper in this issue.

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