specific conductance, (Figure 2). These observations have been repeatedly confirmed.

Finally, the system $HgCl_2$–KCl–H_2O presents very different results from the other two. In the first place, the phase diagram is different, there being three double salts and hence five solubility curves. The equilibrium diagrams at 25 and 34 °C are reported in ref 3, but the reference for 25 °C is incorrect and therefore the author has not been able to consult the original. However, the work described for 34 °C (*7*) was done with meticulous care, leaving no doubt as to the existence of the double salts. The solubilities of this paper cooroborate those given for 25 °C and hence the formulas of the double salts were assumed to be those published.

The viscosities of the saturated solutions are plotted in Figure 3, together with those of mercuric chloride and of potassium chloride alone. In this system, where the solid phase changes, the viscosities plotted vs. molarity of potassium chloride yield a saw-toothed curve which shows some correlation with the nature of the solid phase. This suggests that the nature of the species in solution changes as the solid phase changes. When plotted vs. molarity of mercuric chloride or vs. total molarity, the same discontinuities in viscosity occur with change in solid phase. The viscosities are always greater in the saturated solution than in potassium chloride solutions of the same molarity. The specific conductances are always somewhat lower than the corresponding potassium chloride values.

When the products of specific conductance and viscosity of the saturated solutions are plotted against molarity of KCl, there is an approximately linear increase: the discontinuity accompanying change of solid phase has disappeared (Figure 4). The same behavior is observed for potassium chloride solutions of the same molarity. If the ratio of these products, viz., $\kappa\eta_{\mathrm{mix}}/\kappa\eta_{\mathrm{KCl}}$, is calculated, it is found to be close to unity regardless of the nature of the solid phase. This means that while the product alters with concentration, in the saturated solutions and in the potassium chloride solutions, it does so to the same extent and is independent of the nature of the solid phases. This behavior is not observed with the other two systems. See Table VI, where the ratios are given for all three systems.

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Isobaric Vapor–Liquid Equilibria of the *p*-Xylene–1,2-Dichloroethane System

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The vapor–liquid equilibria of the *p*-xylene–1,2-dichloroethane system were measured at 685 mmHg pressure. Vapor-pressure data in the range of 500–2700 mmHg are also reported. The results on enthalpy of mixing and vapor–liquid equilibria show that system behaves like an ideal system.

This first paper in a series on the vapor–liquid equilibrium data of *p*-xylene–chloroethane systems presents data for the *p*-xylene–1,2-dichloroethane system. Vapor–liquid equilibrium data, apart from their utility in distillation, are required to fill gaps in such important prediction methods as the UNIFAC method.

Experimental Section

Apparatus. A modified Brown still was used to collect the data. The apparatus consisted of a boiler tapered gradually to a Cottrell pump as shown in Figure 1. The boiler was heated with a nichrome wire of 60-Ω resistance. A similar heating wire was wound over the entire length of the Cottrell pump and the separating chamber. The internal heater was made of fine nichrome wire of 1.3-Ω resistance fused to tungsten leads. Figures 2 and 3 show the details of the sample trap and the monostat manometer arrangement. A cathetometer used to read the manometer allowed pressures to be read to ±0.1 mm Hg.

Purity of Materials. *p*-Xylene supplied by M/S E. Merck, Darmstadt, West Germany, was tested for thiophene, dried with phosphorus pentoxide, and then distilled twice in a 150-cm packed column. The middle fraction of the second distillation boiling at a constant temperature of 407.45 K (at 685 mmHg pressure) was collected and stored in clean, dry, amber-colored bottles.

Laboratory-grade 1,2-dichloroethane supplied by M/S BDH, Bombary, India, was washed with a dilute solution of potassium hydroxide and then with distilled water. It was then dried over phosphorus pentoxide and distilled twice. The middle fraction of the second distillation boiling at 353.15 K (at 685 mmHg) was collected and stored in amber-colored bottles. The purified substances were checked for purity by refractive index, density, boiling point at 760 mmHg, chromatograms (obtained by using an AIMIL-NCI dual-column gas chromatograph with a flame ionization detector), and NMR (obtained by using a Varian TC 60 NMR spectrometer). The purity of *p*-xylene was also checked by taking its IR spectra with a Carl Zeiss URIO spectrometer. The physical properties are tabulated in Table

Table I. Physical Properties of Chemicals

substance	refractive index[a] exptl	refractive index[a] lit.	density,[a] g exptl	density,[a] g lit.	bp, K exptl	bp, K lit.
p-xylene	1.4905	1.4904 (*12*)	0.8527	0.8524 (*12*)	411.45	411.50 (*12*)
1,2-dichloroethane	1.4390	1.4392 (*13*)	1.2391	1.2390 (*13*)	356.65	356.63 (*14*)

[a] Refractive index and density measured at 303.15 ± 0.05 K. Accuracy, ±0.0001.

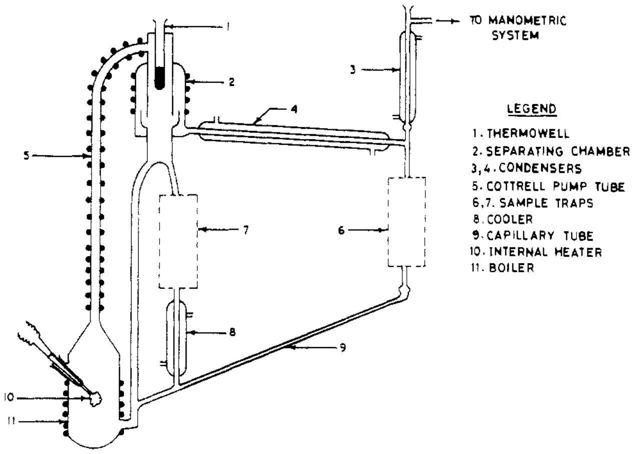

Figure 1. Schematic diagram of the vapor–liquid equilibrium still.

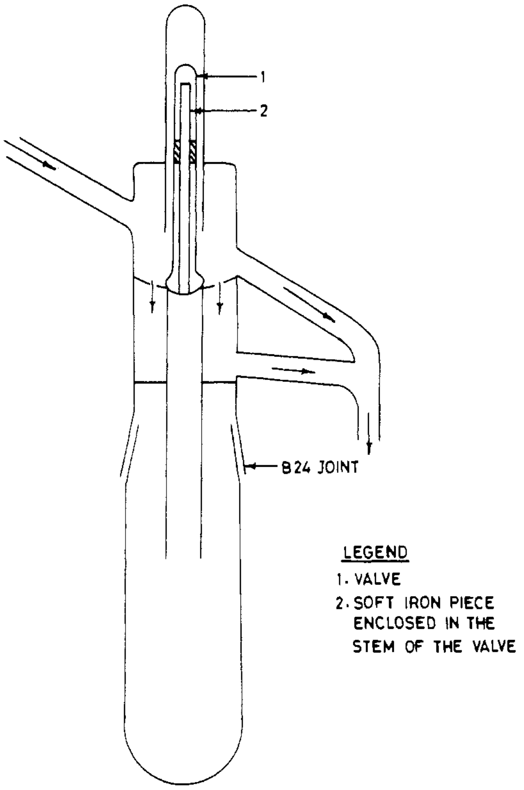

Figure 2. Details of the sample trap.

I. With all of the properties measured, the purity of the liquids was assessed to be better than 99.99 mol %.

Vapor-Liquid Equilibrim Data. Trial runs were conducted with the system toluene–1,2-dichloroethane to establish the functioning of the still, heat inputs, and reproducibility of the results.

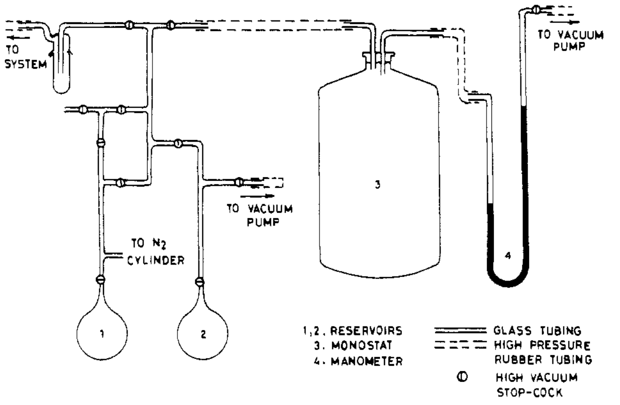

Figure 3. Monostat and manometer arrangement for the vapor–liquid equilibrium still.

Table II. Refractive Index–Composition for the System *p*-Xylene–1,2-Dichloroethane at 303.15 ± 0.05 K

mole fraction *p*-xylene	refractive index	mole fraction *p*-xylene	refractive index
0.0000	1.4390	0.4504	1.4652
0.0248	1.4403	0.4691	1.4663
0.0482	1.4416	0.5285	1.4693
0.0796	1.4441	0.6091	1.4730
0.1244	1.4468	0.6418	1.4750
0.1353	1.4473	0.6893	1.4769
0.1733	1.4495	0.7046	1.4778
0.2084	1.4517	0.7270	1.4788
0.2311	1.4532	0.7672	1.4804
0.2849	1.4560	0.8136	1.4825
0.3178	1.4582	0.8530	1.4842
0.3258	1.4587	0.8983	1.4862
0.3329	1.4591	0.9057	1.4864
0.3610	1.4603	0.9557	1.4885
0.3837	1.4619	0.9803	1.4895
0.4387	1.4645	1.0000	1.4905

Table III. Vapor-Liquid Equilibrium Data for *p*-Xylene-1,2-Dichloroethane System at 685 mmHg

T, K	X_1	Y_1	γ_1	γ_2	Z_1	Z_2
354.25	0.0420	0.0076	0.9661	0.9991	0.9540	1.0010
355.50	0.0880	0.0166	0.9611	1.0037	0.9544	1.0021
357.45	0.1555	0.0320	0.9760	1.0094	0.9555	1.0042
360.05	0.2345	0.0545	1.0025	1.0010	0.9570	1.0069
363.65	0.3340	0.0855	0.9720	1.0006	0.9593	1.0110
366.85	0.4125	0.1200	0.9880	0.9960	0.9614	1.0150
369.65	0.4780	0.1555	1.0044	0.9950	0.9633	1.0178
373.25	0.5520	0.2000	0.9924	0.9994	0.9660	1.0220
378.55	0.6500	0.2820	1.0014	0.9968	0.9700	1.0280
382.15	0.7055	0.3405	0.9953	0.9923	0.9732	1.0331
385.15	0.7500	0.4000	1.0033	0.9864	0.9758	1.0372
390.45	0.8170	0.4985	0.9804	0.9921	0.9810	1.0400
393.85	0.8580	0.5795	0.9840	0.9885	0.9843	1.0480
396.65	0.8950	0.6620	0.9950	1.0060	0.9872	1.0530
400.05	0.9310	0.7620	1.0020	0.9970	0.9910	1.0560
405.15	0.9795	0.9210	1.0030	0.9964	0.9970	1.0592

The boiler was filled with 240 cm^3 of a mixture of known composition. The composition of the mixtures was established by using refractive index. The power input to the internal heater was set at ~5 W and the condensate rate was ~3 cm^3 min^{-1}. The vaporization and condensation rates maintained the liquid level above the heater surface. The refractive index–composition data measured at 303.15 K and presented in Table II fit the equation

$$n^{30}_{D} = 1.438787 + 0.066064X_1 - 0.0177438X_1^2 + 0.00032578X_1^3 \quad (1)$$

with an average absolute deviation of 0.009% and a maximum deviation of 0.02%.

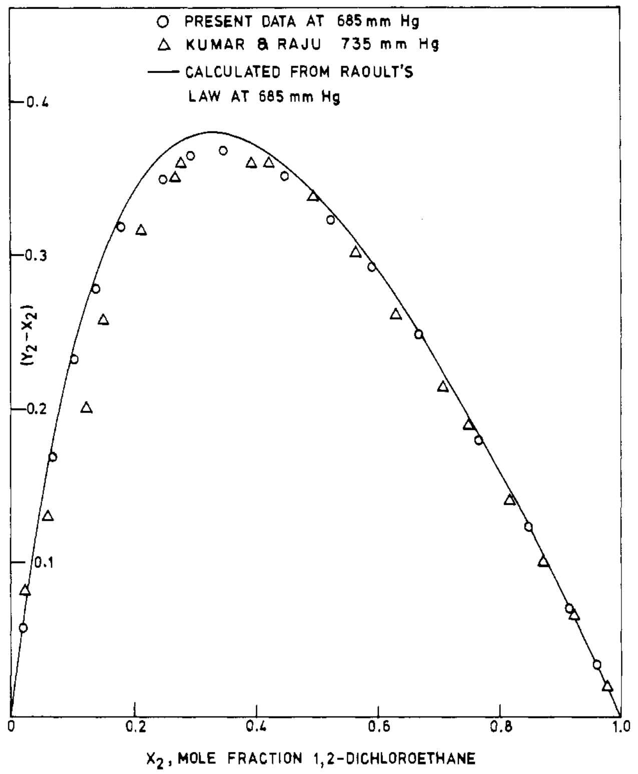

Figure 4. $Y_2 - X_2$ vs. X_2 diagram for *p*-xylene–1,2-dichloroethane system.

Results

The vapor–liquid equilibrium data are pesented in Table III. Table III also lists the activity coefficients and vapor-phase imperfections.

The data were checked for consistency by using eq 2. The

$$\int_0^1 \log (\gamma_1/\gamma_2)\, dX_1 - \int_0^1 H^E/(2.303RT^2)(dT/dX_1)\, dX_1 = 0 \quad (2)$$

values of H^E (*1*) obtained at 308.15 K were used to evaluate the second term of eq 2. The data were also checked according to Herington's test. The bubble point–composition (T–X) data were fitted to eq 3. The values of dT/dX_1 were

$$T = 352.869 + 30.194X_1 - 2.904X_1^2 + 26.950X_1^3 \quad (3)$$

obtained by using eq 3. Equation 3 fits the T–X data with an average absolute deviation of 0.03%. Both of these tests showed that the data are thermodynamically consistent.

The activity-coefficient data presented in Table III show that the system is very close to ideality. This is exemplified as shown in Figure 4, where $Y_2 - X_2$ values are plotted against X_2 together with the Raoult's law values and available literature data (*2*). The ideal behavior of the system was also evident in the excess-enthalpy values which ranged from −125 to 65 J mol^{-1} at 298.15 K and −60 to +110 J mol^{-1} at 303.15 K, increasing with mole fraction of 1,2-dichloroethane.

The values of the activity coefficients were evaluated according to the relations

$$\log \gamma_1 = \log (Y_1P/X_1P_1^0) + 0.4342 \ln Z_1 \quad (4)$$

$$\log \gamma_2 = \log (Y_2P/X_2P_2^0) + 0.4342 \ln Z_2 \quad (5)$$

where

$$Z_1 = \exp\{[(P - P_1^0)(B_{11} - V_1^L) + PY_2^2\delta_{12}]/RT\} \quad (6)$$

$$Z_2 = \exp\{[(P - P_2^0)(B_{22} - V_2^L) + PY_1^2\delta_{12}]/RT\} \quad (7)$$

Table IV. Experimental Vapor Pressures of 1,2-Dichloroethane

T, K	P_2^0, mmHg	T, K	P_2^0, mmHg
344.60	514.1	383.55	1655.0
346.70	548.2	384.35	1688.8
350.45	626.0	385.55	1741.5
352.15	662.1	386.15	1771.7
353.15	685.0	387.25	1820.0
354.75	720.0	388.45	1876.7
356.65	760.0	388.95	1896.5
357.55	781.5	389.65	1934.0
358.65	812.5	390.35	1964.5
360.55	864.5	390.55	1979.6
363.75	949.5	391.45	2023.6
365.35	998.5	391.85	2040.5
366.95	1046.0	392.25	2065.0
368.25	1086.0	393.25	2119.6
369.65	1128.2	394.35	2177.0
371.15	1180.5	394.50	2192.6
371.95	1203.0	395.50	2243.6
373.25	1250.5	396.35	2290.5
374.35	1285.2	396.65	2314.5
374.85	1302.7	396.90	2321.4
376.55	1366.0	397.25	2345.2
377.35	1403.0	397.95	2382.0
378.45	1441.6	398.35	2406.4
378.50	1445.2	399.15	2450.0
378.85	1460.5	399.85	2503.5
380.45	1522.2	400.95	2564.3
380.65	1534.0	401.45	2601.0
381.75	1576.5	402.25	2639.3
382.35	1603.7	403.15	2701.8
382.85	1624.0		

The values of vapor pressure, second virial coefficients, and cross coefficients required in eq 6 and 7 were evaluated as described below.

Vapor Pressures of the Pure Components. The vapor pressures of *p*-xylene were calculated by using the Antoine equation with constants reported in API (*3*) tables.

$$\log P_1^0 = 6.99052 - 1453.43/(T - 57.843) \quad (8)$$

Vapor pressures of 1,2-dichloroethane were measured by using a modified Brown still for pressures up to 685 mmHg. For higher pressures a Swietoslawsky-type still was used. Experimental data are presented in Table IV. The data were fitted to the equation

$$\log P_2^0/P_c = \sum_{j=1}^{5} a_j[(T_c/T) - 1.0]^{j/2} \quad (9)$$

with the coefficients $a_1 = 28.4491$, $a_2 = -162.6535$, $a_3 = 317.2562$, $a_4 = -284.5315$, and $a_5 = 94.6056$. Equation 9 gave an average absolute deviation of 0.16% and a maximum deviation of 0.59% for the 59 experimental points. The data are presented graphically in Figure 5. The available literature data (*4*–*7*) are also shown in Figure 5.

Second Virial Coefficients of the Pure Components. Cox and Andon reported the experimental values of second virial coefficients for *p*-xylene in the temperature range of 377.15–423.15 K. However, in the range of 343.15–423.15 K, the values calculated from the Tsonopoulos equation along with the data of Cox and Andon (*8*) were used. The correlation of Tsonopoulos (*9*) was found to fit the reported data. For 1,2-dichloroethane the values have been reported by Bohmhammel and Mannchen (*10*).

Cross Coefficients, B_{12}. In order to obtain accurate values for B_{12}, in the absence of experimental data, it is necessary to find a potential energy function which can represent accurately the second virial coefficients of pure substances. Then as B_{12} represents values for mixtures of molecules of similar size and chemical nature, the same potential energy function

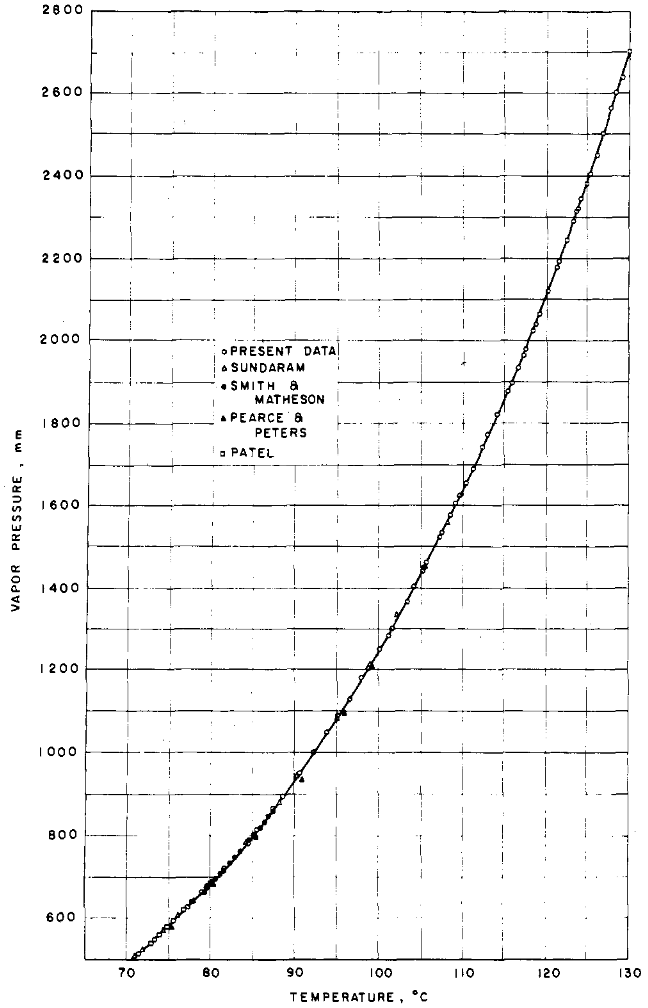

Figure 5. Vapor pressure–temperature for 1,2-dichloroethane.

can be used to derive B_{12} values. With this in mind and the ability of the three-term function

$$\phi(r) = a/r^{18} + b/r^{12} + c/r^{6} \qquad (10)$$

to represent virial coefficients of substances of different chemical nature, eq 10 was used. The constants were evaluated by using the following relations: $\phi(\sigma) = 0$; $\phi(r_m) = -\epsilon$; and $d\phi(r)/dr = 0$ at $r = r_m$. Further, it is assumed that $r_m = K\sigma$. Details of the evaluation of reduced second virial coefficients and the application of eq 10 are given elsewhere (*11*).

The three-term potential with $K = 1.098$ represented very well the experimental second virial coefficients of *p*-xylene and 1,2-dichloroethane in the temperature range of 343.15–423.15 K. The reduced second virial coefficients $B^*(T^*)$ for $K = 1.098$ fit eq 11 with an average absolute deviation of 0.004% and a

$$B^*(T^*) = 0.64154 - 1.3572(1/T^*) - 1.2910(1/T^*)^2 + 0.29652(1/T^*)^3 - 0.11677(1/T^*)^4 \qquad (11)$$

maximum deviation of 0.009%. The values of the force constants obtained are as follows: for *p*-xylene, $\epsilon/k = 645$ K and $\sigma = 6.810$ Å; for 1,2-dichloroethane, $\epsilon/k = 474.26$ K and $\sigma = 5.928$ Å. The values of B_{12} were obtained by using arithmetic and geometric averages for σ_{12} and ϵ_{12}, respectively.

The data obtained as described above were used to calculate activity coefficients and vapor-phase nonidealities by using eq 4–7.

Glossary

B	second virial coefficient
H^E	excess enthalpy
P	pressure
T	temperature
X	mole fraction in liquid
V	liquid molar volume
Y	mole fraction in vapor
Z	vapor-phase imperfection
a, b, c	constants in eq 10
a_j	constants in eq 9
r	distance of separation

Greek Leters

δ	$2B_{12} - B_{11} - B_{22}$
γ	activity coefficient
ϕ	potential function
ϵ	minimum potential energy

Subscripts

1	*p*-xylene
2	1,2-dichloroethane
12	interaction coefficient

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