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

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Isobaric vapor–liquid equilibria of the *p*-xylene–1,1,2,2-tetrachloroethane system were measured at 685-mmHg pressure. Activity coefficients were evaluated and correlated.

This third paper on the vapor–liquid equilibria of *p*-xylene–chloroethane systems reports the data for the *p*-xylene–1,1,2,2-tetrachloroethane system. Data on 1,1,2,2-tetrachloroethane with benzene and toluene have been reported earlier (*1*, *2*). Data on *p*-xylene with 1,2-dichloroethane and 1,1,1-trichloroethane have also been reported (*3*, *4*).

Experimental Section

The vapor–liquid equilibrium data were collected by using a modified Brown still. A detailed description and operation of the apparatus can be found elsewhere (*3*). Analar and laboratory-grade chemicals were purified as described earlier (*3*) and the purities of the chemicals were assessed by measuring their physical properties and also by taking NMR spectra (using a Varian TC 60 NMR spectrometer) and vapor-phase chromatograms (using AIMIL-NCL dual-column gas chromatograph with FI detecter). The density and the refractive index at 303.15 K of 1,1,2,2-tetrachloroethane were 1.5784 g cm^{-3} and 1.4889, respectively, compared to the literature values of 1.5786 g cm^{-3} (*5*) and 1.4884 (*5*). The normal boiling temperature was 419.45 K compared to the literature value of 419.35 K (*5*). The properties of *p*-xylene were given earlier (*3*, *4*). The purity of the chemicals is assessed to be better than 99.9 mol %. As the refractive indices of the two substances are very close, the composition of the liquid and the condensed vapor were determined by density measurements carried out at 303.15 ± 0.05 K. The density–composition data presented in Table I fit the equation

$$\rho\ (\text{g cm}^{-3},\ 30\ ^\circ\text{C}) = 1.5777 - 0.828077X + 0.102972X_1^2 \tag{1}$$

with an average absolute deviation of 0.045% and a maximum deviation of 0.21%.

Table I. Density–Composition of *p*-Xylene–1,1,2,2-Tetrachloroethane Mixtures at 303.15 ± 0.05 K

X_1[a]	ρ,[b] g cm^{-3}	X_1[a]	ρ,[b] g cm^{-3}
0.0	1.5784	0.4920	1.1950
0.0260	1.5540	0.5392	1.1620
0.0467	1.5411	0.6148	1.1080
0.0902	1.5045	0.6340	1.0944
0.1260	1.4749	0.7050	1.0453
0.1455	1.4594	0.7530	1.0125
0.2010	1.4149	0.7920	0.9873
0.2364	1.3872	0.8415	0.9518
0.2932	1.3437	0.8990	0.9170
0.3462	1.3034	0.9500	0.8840
0.3965	1.2654	1.000	0.8527
0.4390	1.2336		

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

Table II. Vapor–Liquid Equilibrium Data of *p*-Xylene–1,1,2,2-Tetrachloroethane at 685 mmHg

T, K	X_1	Y_1	Z_1	Z_2	γ_1	γ_2
415.15	0.0450	0.0480	1.0053	0.9997	0.8763	1.0046
414.70	0.1070	0.1140	1.0053	0.9992	0.8856	1.0120
414.35	0.1570	0.1680	1.0054	0.9988	0.8978	1.0154
414.05	0.2020	0.2160	1.0054	0.9984	0.9042	1.0190
413.75	0.2520	0.2680	1.0054	0.9980	0.9064	1.0230
413.35	0.3020	0.3220	1.0052	0.9975	0.9183	1.0274
413.05	0.3510	0.3780	1.0052	0.9970	0.9348	1.0212
412.75	0.4000	0.4370	1.0051	0.9964	0.9559	1.0095
412.45	0.4470	0.4920	1.0050	0.9960	0.9706	0.9957
412.25	0.4880	0.5400	1.0049	0.9955	0.9810	0.9788
411.85	0.5490	0.6060	1.0046	0.9950	0.9888	0.9619
411.45	0.6020	0.6620	1.0043	0.9943	0.9954	0.9437
411.25	0.6340	0.6945	1.0042	0.9940	0.9967	0.9325
411.05	0.6580	0.7180	1.0040	0.9936	0.9980	0.9262
411.05	0.6600	0.7200	1.0040	0.9936	0.9977	0.9251
410.80	0.6900	0.7500	1.0037	0.9932	1.0006	0.9115
410.65	0.7060	0.7650	1.0036	0.9930	1.0013	0.9071
410.25	0.7520	0.8080	1.0031	0.9923	1.0032	0.8884
410.10	0.7670	0.8220	1.0030	0.9921	1.0045	0.8794
409.75	0.8000	0.8510	1.0026	0.9916	1.0061	0.8660
409.15	0.8560	0.8970	1.0019	0.9910	1.0066	0.8453
408.75	0.8870	0.9210	1.0014	0.9905	1.0079	0.8352
408.45	0.9100	0.9380	1.0010	0.9900	1.0084	0.8300
407.85	0.9620	0.9750	1.0003	0.9892	1.0071	0.8064

Results

The experimentally determined T, X, Y values together with the calculated values of activity coefficients γ_1, γ_2 and the gas-phase imperfections, Z_1, Z_2 (*3*) are tabulated in Table II. Experimental T, X, Y values are shown graphically in Figure 1. The experimental vapor pressure data of 1,1,2,2-tetrachloroethane in the temperature range of 480.15–519.15 K are given in Table III and in Figure 2 along with the literature data. The data fit the equation

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

with an average absolute deviation of 0.23% and a maximum deviation of 0.73%. The constants in eq 2 are a_1 = 125.9957, a_2 = 693.1446, a_3 = 1366.8905, a_4 = −1206.6978, and a_5 = 397.8165. Equation 2 with two extra constants enhances the vapor pressure representation better compared to the Antoine constants tabulated by Driesbach (*6*) and by Zwolinski and co-workers (*7*). The Antoine representation gives an average absolute deviation and a maximum deviation of 0.79% and 2.3% for Driesbach and 2.8% and 3.3% for Zwolinski et al. constants. The ranges covered by the Antoine equations are wider. The experimental data presented in Table III compare very well with the data of Patel et al. and Sundaram and Vis-

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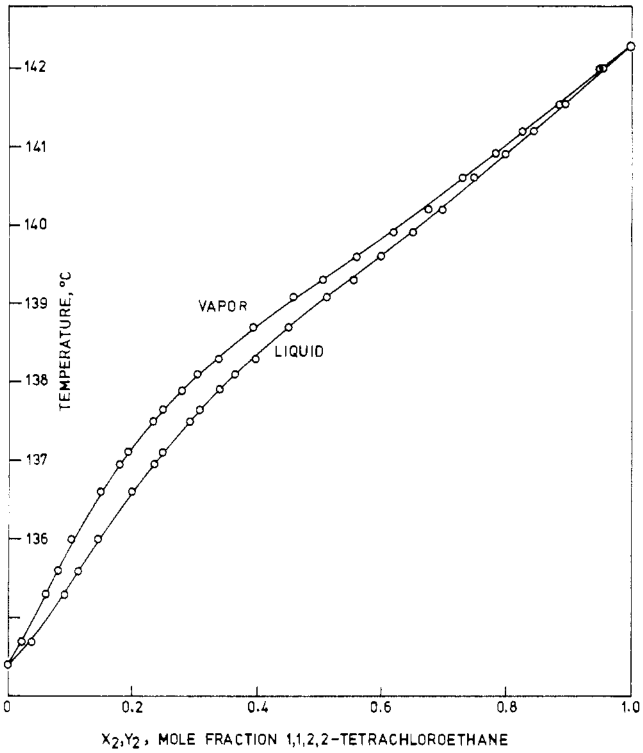

Figure 1. *T-X-Y* diagram for the *p*-xylene–1,1,2,2-tetrachloroethane system.

Table III. Experimental Vapor Pressures of 1,1,2,2-Tetrachloroethane

T, K	$P_2^0{}_{\text{exptl}}$, mmHg	$\delta P_2^{0\,a}$	T, K	$P_2^0{}_{\text{exptl}}$, mmHg	$\delta P_2^{0\,a}$
380.15	232.75	0.14	408.05	554.30	−0.48
384.15	264.70	−0.36	408.90	570.00	−0.11
386.65	287.50	−0.35	409.10	574.00	0.02
389.15	312.20	−0.25	410.45	595.00	−0.19
392.05	343.50	−0.01	411.90	620.50	−0.04
392.40	346.80	−0.16	412.85	634.80	−0.40
394.25	371.00	0.73	413.55	650.00	0.03
395.90	390.00	0.58	414.55	668.00	0.03
399.35	431.50	0.09	415.05	676.00	−0.14
401.35	456.00	−0.41	415.15	677.80	−0.14
403.60	487.20	−0.47	415.50	684.50	0.11
404.95	507.00	−0.45	416.85	712.50	0.24
405.40	513.10	−0.57	418.25	737.50	−0.05
407.10	540.00	−0.37	419.45	760.00	−0.22

[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.

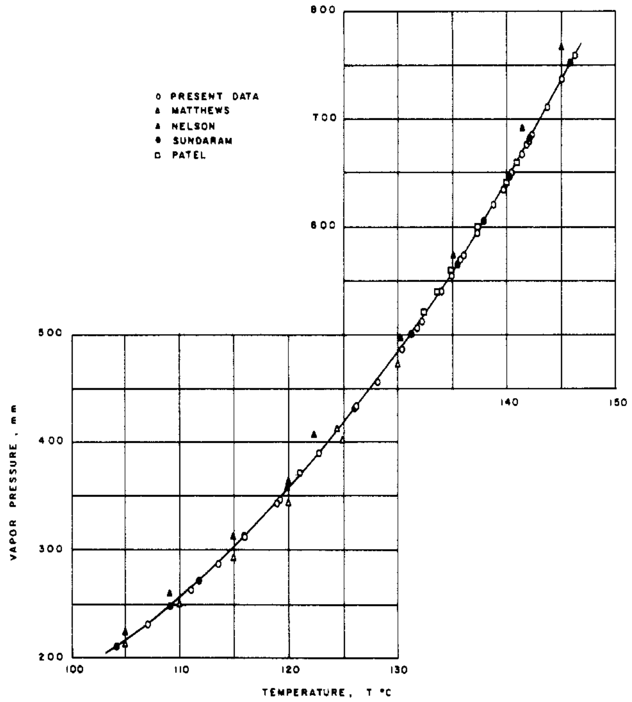

Figure 2. Vapor pressure of 1,1,2,2-tetrachloroethane.

Table IV. Constants for Wilson and Redlich-Kister Correlations and Deviations

correlation	constants	$\delta\gamma_1{}^a$
Wilson	$\Lambda_{12} = 1.3080$ $\Lambda_{21} = 0.8442$	1.58
Redlich-Kister	$A_1 = -0.08686$ $A_2 = -0.09344$ $A_3 = -0.00265$	3.32

[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 data points.

wanath (*8*). The present data however are lower compared with the data of Nelson (*9*) and higher compared with the data of Matthews et al. (*10*).

The second virial coefficients of 1,1,2,2-tetrachloroethane were evaluated by using the corresponding states principle since experimental data are not available. To accomplish this, we fitted the reduced second virial coefficients data, B/V_c, of ethyl chloride, 1,2-dichloroethane, and 1,1,1-trichloroethane to the equation

$$B/V_c = \sum_{j=1}^{5} b_j(T/T_c)^{j-1} \tag{3}$$

Equation 3 with constants $b_1 = 25.208$, $b_2 = -192.116$, $b_3 = 417.455$, $b_4 = 368.737$, and $b_5 = 116.82$ fitted the data with an average absolute deviation of 1.0% and a maximum deviation of 1.7%. The second virial coefficient data for *p*-xylene were reported earlier (*3*, *4*). The interaction virial coefficients were evaluated as described earlier (*3*). The values of the force constants used for 1,1,2,2-tetrachloroethane are $\epsilon/k = 545.8$ K and $\sigma = 6.91$ Å. These data were used to calculate the vapor-phase imperfections and activity coefficients of the two substances using the relations given earlier (*3*).

Correlation of Activity Coefficients

The activity coefficients thus calculated were correlated by using the Wilson equations

$$\ln \gamma_1 = -\ln A + X_2[(\Lambda_{12}/A) - (\Lambda_{21}/B)] \tag{4}$$

$$\ln \gamma_2 = -\ln B - X_1[(\Lambda_{12}/A) - (\Lambda_{21}/B)] \tag{5}$$

where

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

and Redlich-Kister equations

$$\ln \gamma_1 = X_2^2A_1 + A_2(3X_1 - X_2) + A_3(X_1 - X_2)(5X_1 - X_2) \tag{6}$$

$$\ln \gamma_2 = X_1^2A_1 + A_2(X_1 - 3X_2) + A_3(X_1 - X_2)(X_1 - 5X_2) \tag{7}$$

The constants of the equations evaluated by using the least-squares principle are tabulated in Table IV along with a com-

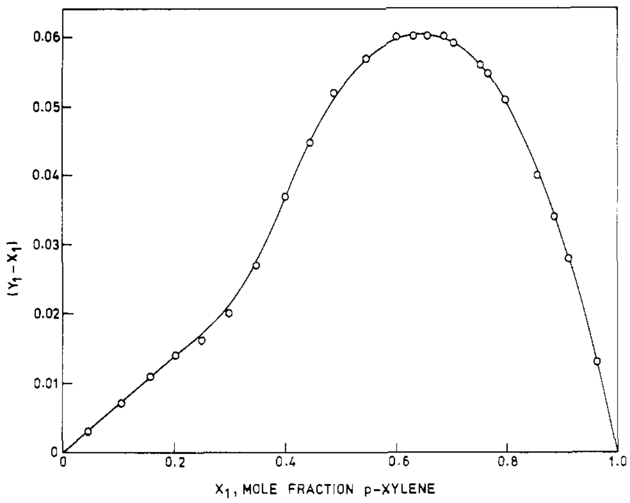

Figure 3. $Y_1 - X_1$ vs. X_1 diagram for the *p*-xylene-tetrachloroethane system.

parison of the two correlations.

Thermodynamic Consistency

The thermodynamic consistency of T-X-Y data has to be tested by using the rigorous Gibbs-Duhem equation

$$I_1 + I_2 + I_3 = 0 \tag{8}$$

where

$$I_1 = \int_0^1 \log (\gamma_1/\gamma_2)\, \mathrm{d}X_1 \tag{9}$$

$$I_2 = -\int_0^1 (H^E/(2.303RT^2)(\mathrm{d}T/\mathrm{d}X_1)\, \mathrm{d}X_1 \tag{10}$$

$$I_3 = \int_0^1 (V^E/RT)(\mathrm{d}P/\mathrm{d}X_1)\, \mathrm{d}X_1 \tag{11}$$

The volume change on mixing for the *p*-xylene-1,1,2,2-tetrachloroethane is negligible. However, the enthalpy of mixing at 308.15 K ranges from -300 J mol^{-1} at X_1 = 0.03 to -600 J mol^{-1} at X_1 = 0.9 with a minimum of -3400 J mol^{-1} at X_1 = 0.36. Similar but slightly higher negative values are obtained at 298.15 K. Therefore, it is essential to consider I_1 and I_2 in testing the thermodynamic consistency of the data. The integral I_1 was evaluated graphically. To evaluate I_2, we fitted the bubble temperature-composition data to the relation

$$T = \sum_{i=1}^{4} B_i x^{i-1} \tag{12}$$

Equation 12 fitted the T-X data with an average absolute deviation of 0.006% and a maximum deviation of 0.01% with B_1 = 415.589, B_2 = -9.109, B_3 = 8.334, and B_4 = -7.553, the constants being evaluated by using the least-squares technique. Using eq 12 to get the necessary derivative, we evaluated I_2 numerically with Simpson's rule. The excess enthalpies of mixing measured at 308.15 K (*4*) were used in evaluating I_2. The values of I_1 and I_2 were 0.005 08 and -0.004 65, respectively, giving a value of 0.000 43 for $I_1 + I_2$ and indicating the consistency of the data. The data were also checked for consistency by using Herington criteria (*11*). It was found that the data are internally consistent with D = 10.63 and J = 2.88, thus giving a value of $D - J < 10$. An error analysis performed on experimental values revealed the maximum errors in γ_1 and γ_2 to be 0.57% and 0.69%, respectively. The errors in pressure, composition, and temperature measurements were ±0.1 mm Hg, ±0.0001, and ±0.05 K, respectively. Figure 3 reveals that there were no random errors. Taking all these into consideration together with the purity of the chemicals, the accuracy of measurements, and the agreement of the vapor pressure data with the literature values, the data presented in this paper should be reliable and accurate.

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Diffusion Coefficients of Acetates in Aqueous Sucrose Solutions

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Diffusivities of ethyl, *n*-propyl, *n*-butyl, and *n*-pentyl acetates in 0-55% w/w solutions of sucrose in water were measured at 25 and 45 °C and high dilution of the acetates by using glass diaphragm cells. The results agree well with previous data, where comparisons can be made. The data are also rationalized in terms of absolute rate theory and the functionality between solute diffusivity and solution viscosity.

Introduction

Relatively few experimental data are available for diffusion coefficients of homologous series of solutes in a given solvent system, or for diffusion coefficients of solutes in aqueous carbohydrate solutions covering a wide range of composition and viscosity. Among other applications, such data are valuable for interpretation of measurements of retention of volatile flavor and aroma components during concentration and drying processes for liquid foods.

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