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Densities of Vinyl Chloride from 5 to 65 °C and Saturation Pressure to 4.2 MPa

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Liquid densities of vinyl chloride have been measured in the temperature range of 5–65 °C and the pressure range of the saturated liquid up to 4.2 MPa. The estimated accuracy of these data is 0.03%. The pressure dependence of the density is predicted within experimental accuracy by an extension of the principle of corresponding states, using ethylene as a reference fluid.

Introduction

Almost 9 × 10^9 lb of vinyl chloride monomer (VCM) was produced in the U.S. in 1978 (*1*). Although a few data for the density of saturated liquid VCM have been reported (*2–5*), there have been no reported data on the pressure dependence of the compressed liquid density under the conditions for which VCM is commonly transported and processed. We here report experimental densities of VCM from 5 to 65 °C and saturation pressures to 4.2 MPa. The experimental data are correlated within experimental error with a Tait equation (*6*, *7*). We then develop a corresponding states treatment for prediction of VCM density.

Experimental Measurements

Samples. Nitrogen was Linde ultrahigh pure grade, 99.99% purity.

Water was bottled, distilled water which was then distilled 2 more times, the second time under vacuum to degas it. The vacuum-distilled water was immediately transferred to a syringe which acted as sample reservoir for the sample line.

Vinyl chloride monomer was obtained in 75-cm^3 sample cylinders from Shell Oil Co.'s Deer Park manufacturing complex. Total GLC impurity analysis was done on each sample. The most impure sample used in this work contained total impurities of 50 ppm and thus had a vinyl chloride monomer purity of 99.995%.

The major impurity was methyl chloride, which has a liquid density approximately 1.4 times greater than VCM at any temperature between 5 and 60 °C. Thus, taking the extreme example of 50 ppm methyl chloride impurity and assuming that the partial molar volumes are the same as the molar volumes of the pure components, one can postulate the density of the mixture as

$$\bar{V} = 0.99995\bar{V}_{\mathrm{VCM}} + 0.00005\bar{V}_{\mathrm{MeCl}} = 0.99995\bar{V}_{\mathrm{VCM}} + 0.00005(1.4)\bar{V}_{\mathrm{VCM}}$$

$$\bar{V} \simeq 1.00002\bar{V}_{\mathrm{VCM}}$$

where $\bar{V}$ is the molar volume and $\bar{V}_{\mathrm{VCM}}$ is the molar volume of VCM. It is clear that the measured VCM density would be affected by only ∼0.002% by 50 ppm methyl chloride impurity, the hypothesized worst case.

Densimeter. A schematic diagram of the densimeter appears in Figure 1. The principle part of the densimeter is the Mettler/Paar DMA602 remote measuring cell, which has been appropriately modified for density measurements up to 4.4 MPa, and the Mettler/Paar DMA60 electronic counter and digital readout instrument. The density determination is based on measuring the period of oscillation of a U-shaped sample tube. The period of oscillation of the DMA602 sample tube is processed by the DMA60 which gives an eight-digit readout of the oscillation period. The sample tube is made of Duran 50 glass, has a volume of 0.7 mL, and is fused into a double-walled glass cylinder. The cavity surrounding the sample tube is filled with a gas of high thermal conductivity. Inside the same cylinder is a capillary tube thermistor well. The entire cylinder is inside a circulating, thermostated water bath.

The measuring principle of the instrument is based on the change in the natural frequency of an oscillator as a function of the total mass of the oscillator. The following relationship exists between the oscillation period, F, and the density, ρ, of the sample:

$$\rho = (1/\mathrm{A})(F^2 - \mathrm{B}) \qquad (1)$$

where A and B are instrument constants which may be determined from calibration measurements of samples of known density. When two different substances whose densities are known are measured, then

$$\rho_1 - \rho_2 = k(F_1^{\,2} - F_2^{\,2}) \qquad (2)$$

where $k = 1/\mathrm{A}$. The factor k is both temperature and pressure dependent. High-purity nitrogen and water were used as calibrating substances from which $k(T,P)$ was derived. The density of VCM was then calculated by eq 2 from measured values of F_{VCM}, T, and P and the correlated values of $F_{\mathrm{H_2O}}(T,P)$, $k(T,P)$, and $\rho_{\mathrm{H_2O}}$.

Temperature Measurement and Control. Temperatures between 5 and 70 °C were measured by using Yellow Springs Instruments, Inc., thermilinear composite thermistors no. 44018 in conjunction with a YSI 741A-10 thermivolt signal conditioner which converts the linear resistance change to a millivolt signal. The millivolt signal was read on a calibrated Data Precision 3500 $5^1/_2$-digit Multimeter. In the temperature range of 0–100 °C, these thermistors have a stated linearity of ±0.22 °C, an absolute accuracy of ±0.4 °C, and a resolution of ±0.001 °C.

Temperature correction calibration curves for each of four thermistors were drawn by comparing the temperature measured with a Leeds and Northrup platinum resistance thermometer with the millivolt reading from the thermistors. The resistance of the platinum thermometer was measured with a Leeds and Northrup Mueller bridge which had been calibrated by Leeds and Northrup. An ice bath was used as the reference point to achieve an absolute temperature accuracy of ±0.01 °C for the platinum thermometer. The thermistor temperature corrections ranged from approximately 0.1 to 0.6 °C between 5 and 70 °C. The accuracy of corrected thermistor temperature readings is estimated to be ±0.1 °C. An error of 0.1 °C in the temperature yields an uncertainty in the density determination on the order of 2.5 × 10^{-4} g/cm^3, or ∼0.025% of the density.

The temperature of the sample was controlled with a circulating, thermostated water bath, Hotpack 334. The temperature

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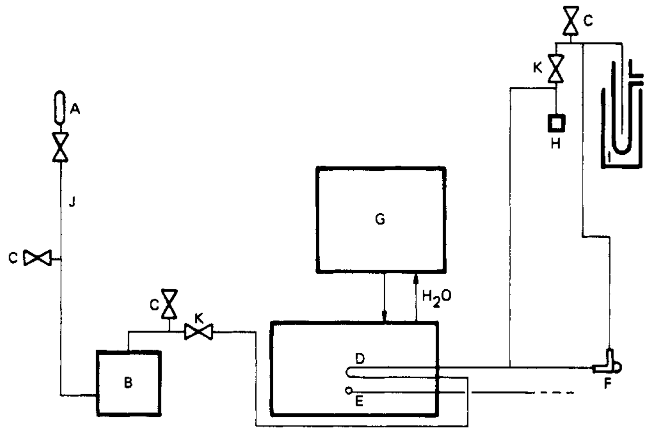

Figure 1. Schematic diagram of the density measurement apparatus: (A) sample cylinder; (B) Waters and Associates liquid pump; (C) dry nitrogen purge line; (D) DMA602HP density measurement cell (volume of cell = 0.7 mL); (E) thermistor (YSI 44018X); (F) pressure relief valve (4.5 MPa); (G) circulating water constant-temperature bath Hotpack 334; (H) pressure transducer (Sensotec TJE series); (I) liquid-nitrogen trap; (J) stainless-steel tube (0.04-in. i.d.); (K) valves (13.8 MPa, 0.093 × 1.6 in. orifice).

in the sample cell generally stayed constant within 0.002 °C for a measurement at one pressure (a few minutes) and within 0.01 °C for a measurement series (several hours).

Pressure Measurement and Control. The absolute pressure was measured by using a Sensotec differential TJE series transducer in conjunction with a Doric Scientific series 420 digital transducer indicator. The transducer was calibrated against two overlapping, calibrated Heise gauges (0–1000 psia, ±0.1% full scale accuracy; 0–100 psia, ±0.1% full scale accuracy). The pressure measurements were accurate to within ±7 kPa between 3.4 and 4.5 MPa. An error of 7 kPa in the pressure determination affects the liquid vinyl chloride density determination by approximately 2×10^{-5} g/cm^3, or ~0.002% of the density.

Pressure generation and control was manifested by different techniques depending on the sample: for water, a Waters and Associates Model 6000 solvent delivery system was used; for nitrogen, a gas pressure regulator was used; and for VCM, a hydrostatic method was used. The Waters solvent pump could not be used with VCM because the VCM dissolved one of the pump gaskets. VCM was loaded into the sample line (cf. Figure 1) using its own vapor pressure at 60 °C (~1.1 MPa). The VCM sample cylinder was heated to 60 °C with heating tape before the cylinder was opened to the evacuated sample line. Once the line was filled, the cylinder valve was shut to create a hydrostatic system. The VCM pressure was then generated and controlled by heating the sample line. For a measurement series at one pressure setting, the pressure generally remained constant within 3 kPa. A change in the sample line temperature had no measurable effect on the temperature in the thermostated DMA602 sample tube. A sample line temperature of approximately 45 °C produced a sample pressure of 4.1 MPa.

Calibration of Densimeter. As described above, the densimeter can be used to measure an unknown density of a substance when both the density of another substance and the instrument *k* factor are known as functions of temperature and pressure.

Water and nitrogen were used as calibrating substances. The period of oscillation of each was measured at 5 °C intervals of temperature between 5 and 70 °C and at 0.3-MPa intervals of pressure between 0.1 and 4.2 MPa. The periods of oscillation of each substance were then fitted to polynomial functions of temperature and pressure. For H_2O, the period of oscillation in seconds was described by the function

$$F_{H_2O} = a + bP + cP^2 \qquad (3)$$

where

$$a = c_1 + c_2T + c_3T^2$$
$$b = c_4 + c_5T + c_6T^2$$
$$c = c_7$$

The fitted equation reproduced experimental oscillation periods to less than 0.001%.

The *k* factor from eq 2 was then calculated at each temperature and pressure at which an oscillation period for nitrogen was measured. The densities of water and nitrogen at each temperature and pressure were calculated from an equation of state which represents experimental measurements to within 0.001% (*8*, *9*) and to less than 0.1% (*10*), respectively. The experimentally derived *k* factors were then fitted to a polynomial function

$$k(T,P) = a + bP + cP^2 \qquad (4)$$

where *a*, *b*, and *c* are functions of temperature. The average of the differences between experimental *k* factors and those calculated from the eq 4 correlation is 0.002%.

In summary, combining the uncertainties in the known water and nitrogen densities, the uncertainty in F_{H_2O}, and the error in the correlated *k* factor results in a 0.005% error in a VCM density found by using eq 2 and a measured period of oscillation for VCM.

The primary instrument calibration was completed before any VCM measurements. However, a series of "spot-check" calibration measurements with water and nitrogen were made after ~75% of the VCM measurements had been completed. These calibration measurements repeated the previously measured periods of oscillation within 0.001% for water and 0.002% for nitrogen.

Experimental Uncertainties and Repeatability. At each experimental temperature and pressure, three measurements of F_{VCM} were obtained. These generally agreed within 1 part in 10^7. The experimental data in Table I at each temperature are listed in the order in which they were obtained. Note, for example, at 22.8 °C agreement between values at 2.144 MPa compared with 2.150 MPa, and 2.473 MPa compared with 2.461 MPa at 22.8 °C.

From the above discussion, the largest contribution to experimental uncertainty is the temperature uncertainty which contributes 0.025% error to a measured density. The calibration error contributes another 0.005% and error in pressure measurement adds an additional 0.002% for a total estimated uncertainty of 0.032% for the experimental liquid densities.

It should be noted that the density of VCM is close to that of the reference fluid water, which provides for instrument calibration at the stated accuracy.

Results

Vinyl chloride densities as determined from the measured periods of oscillation of the DMA602, as described above, are listed in Table I. These measured densities cover the temperature range of 8–65 °C and pressure range of near saturation (~0.4 MPa) to 4.2 MPa.

The experimental densities were fitted to a pseudo-Tait equation (*6*, *7*) of the form

$$\rho_\sigma(T)/\rho(T,P) = 1.0 - A(T)\,\rho_\sigma(T)\ln\{[B(T) + P]/[B(T) + P_\sigma(T)]\} \qquad (5)$$

where $\rho(T,P)$ designates the density at temperature *T* and pressure *P*, $\rho_\sigma(T)$ is the density at the saturation pressure at temperature *T*, $P_\sigma(T)$ is the saturation pressure at *T*, and $A(T)$ and $B(T)$ are temperature-dependent coefficients. A value for *A* at each temperature was found from a fit of eq 5 to the

Table I. Liquid Vinyl Chloride Experimental and Correlated Densities

temp, °C	P, MPa	exptl density, kg/m^3	exptl vs. Tait equation deviation,[a] %
7.84	0.456	932.38	−0.012
7.84	1.085	933.49	−0.012
7.84	1.347	933.95	−0.013
7.84	1.857	934.85	−0.013
7.84	2.171	935.39	−0.012
7.84	2.654	936.24	−0.012
7.84	3.236	937.25	−0.012
7.84	3.552	937.79	−0.012
7.84	3.746	938.12	−0.012
8.33	0.421	931.44	−0.010
8.33	0.849	932.21	−0.009
8.33	1.371	933.16	−0.009
8.33	2.377	934.93	−0.008
8.33	3.037	936.08	−0.008
8.33	3.889	937.55	−0.007
16.81	0.383	916.11	0.022
16.81	0.658	916.66	0.023
16.81	1.445	918.21	0.023
16.81	2.122	919.50	0.021
16.81	3.151	921.42	0.016
16.81	3.882	922.79	0.017
22.28	0.453	905.97	0.016
22.28	1.034	907.19	0.016
22.28	1.053	907.27	0.021
22.28	1.058	907.24	0.016
22.28	1.493	908.14	0.016
22.28	1.600	908.37	0.017
22.28	1.939	909.06	0.016
22.28	2.144	909.49	0.017
22.28	2.150	909.50	0.017
22.28	2.461	910.13	0.017
22.28	2.473	910.26	0.028
22.28	2.860	910.93	0.016
22.28	3.017	911.26	0.017
22.28	3.483	912.19	0.017
22.28	3.859	912.93	0.017
22.28	4.078	913.36	0.016
33.19	0.721	885.70	0.023
33.19	1.425	887.40	0.025
33.19	2.110	889.01	0.025
33.19	2.956	890.96	0.025
33.19	3.756	892.78	0.026
45.25	1.015	882.11	−0.010
45.25	1.121	862.60	−0.014
45.25	1.128	862.42	−0.011
45.25	1.607	863.75	−0.012
45.25	1.640	863.85	−0.011
45.25	1.764	864.18	−0.012
45.25	1.928	864.64	−0.011
45.25	1.981	864.78	−0.011
45.25	2.688	866.71	−0.010
45.25	2.690	866.71	−0.010
45.25	3.010	867.56	−0.011
45.25	3.084	867.77	−0.010
45.25	3.176	868.00	−0.011
45.25	3.384	868.56	−0.009
45.25	3.414	868.61	−0.013
45.25	3.671	869.32	−0.009
45.25	3.699	869.34	−0.013
45.25	3.707	869.41	−0.009
45.25	4.093	870.41	−0.010
64.10	1.108	822.00	−0.009
64.10	1.771	824.46	−0.009
64.10	1.793	824.54	−0.010
64.10	1.804	824.56	−0.013
64.10	2.228	826.11	0.012
64.10	2.230	826.14	0.010
64.10	3.092	829.21	0.009
64.10	3.782	831.56	0.013

[a] 100(experimental density − Tait equation density)/experimental density.

Table II. Coefficients Fitted to the Modified Tait Equation for Liquid Vinyl Chloride Monomer and Extrapolated Saturated Liquid Densities

temp, °C	10^3A, m^3/kg	B, MPa	10^3(av deviation),[a] %	ρ_σ,[b] kg/m^3
7.84	0.098 841 904	47.380 91	0.6	931.96
8.33	0.099 280 921	47.096 16	0.2	931.10
16.81	0.099 995 330	42.275 90	1.1	915.97
22.28	0.102 321 541	39.274 64	1.7	905.79
33.19	0.105 396 292	33.541 61	0.3	885.17
45.25	0.108 366 458	27.596 47	1.0	861.19
64.10	0.112 919 116	19.129 05	1.1	821.96

[a] Average percent deviation = $\Sigma_{i=1}^{N}[100(\rho_i^{\text{exptl}} - \rho_i^{\text{Tait}})/\rho_i^{\text{exptl}}]/N$ where ρ is the density. [b] Saturated liquid density calculated from fit of experimental data to eq 8.

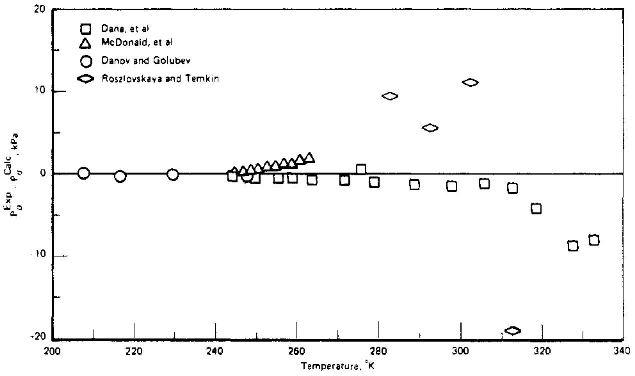

Figure 2. Comparison of experimental and correlated vapor pressures for vinyl chloride.

experimental data. The value for the B coefficient at each temperature was taken to be the same as the coefficient B estimated from a corresponding states prediction of the density, to be discussed below. The values of A and B at each temperature are listed in Table II along with the average of the percentage deviations between the experimental densities and those densities calculated from the fit to eq 5. The deviations average 0.001% and none are greater than 0.002%, confirming that the choice of B in each case was adequate. The A and B coefficients from the isothermal fits were then fitted to polynomial functions of temperature as

$$A(T),\ \text{m}^3/\text{kg} = 0.40067251 \times 10^{-4} + (0.17061321 \times 10^{-6})T + (0.135797794 \times 10^{-9})T^2 \quad (6)$$

$$B(T),\ \text{MPa} = 0.3226531394 \times 10^{3} - (0.1377488302 \times 10^{1})T + (0.1415821752 \times 10^{-2})T^2 \quad (7)$$

The densities at saturation pressures were fitted to a modified Yen–Woods (*11*) expression

$$\rho_\sigma^*(T) = 1.0 + 2.121515455(1.0 - T^*)^{1/3} - 0.034480(1 - T^*)^{2/3} + 0.8138014(1 - T^*)^{4/3} \quad (8)$$

where * indicates that property is reduced by the corresponding critical property.

The experimental vinyl chloride vapor pressures (*12–15*) were fitted to a reduced form of the Frost–Kalkwarf (*11*) equation

$$\ln P_\sigma^*(T) = 9.242386(1.0 - 1.0/T^*) - 4.6576315 \ln T^* + (27/64)(P_\sigma^*/T^{*2} - 1.0) \quad (9)$$

The average percentage deviation between the correlated (eq 9) and experimental saturation pressures is ~1.4 kPa (cf. Figure 2). Using the values of $A(T)$, $B(T)$, and $P_\sigma(T)$ in eq 5 yields calculated densities as a function of temperature and pressure, which are compared with experimental densities in

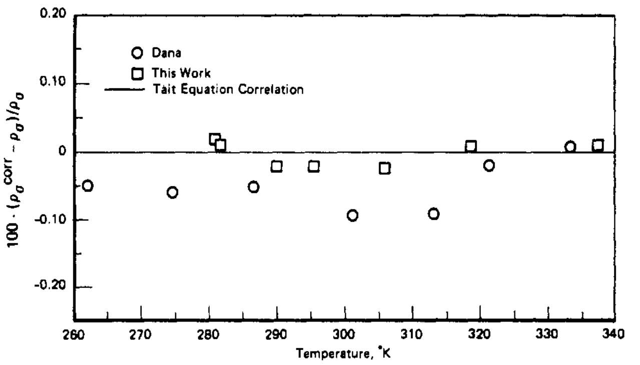

Figure 3. Comparison of experimental and correlated saturated liquid densities of vinyl chloride.

Table I. The percentage deviations between experimental and correlated densities as listed in Table I average 0.015% with none greater than 0.028%, which is within the estimated experimental uncertainty.

Discussion

A review of the literature yielded only one previous report of measurements of vinyl chloride densities (*2*), although a few other isolated values have appeared in data tabulations (*3*, *4*). However, the previously reported densities are at saturation pressures only. Dana (*2*) measured saturated liquid densities from −13 to +60 °C with an uncertainty of ±0.1%. Figure 3 contains a comparison of saturated liquid densities from this work (Table II) and those measured by Dana. The zero line represents the saturation densities from eq 7. The average deviation between Dana's values and this work is (−)0.05% and the largest deviation is (−)0.09%, within the accuracy of the Dana data, 0.1%.

Density Prediction from Corresponding States

Because of the fact that no experimental data on VCM-density pressure dependence existed when we began this work, it was decided that the effect of pressure on the liquid density would be estimated by using the extended principle of corresponding states. The first step in this procedure is the estimation of the critical temperature, pressure, and volume—none of which have been experimentally measured.

The critical temperature was estimated by using three different procedures. The first method was to assume that the ratio of the critical temperature of VCM to that of ethylene was the same as the ratio of ethyl chloride to ethane. This estimation procedure leads to a value of 425.6 K.

The second method employed was that due to Lyderson (*16*), which estimates the ratio of the normal boiling point to the critical temperature on the basis of molecular structure. Assuming a boiling point of 259.4 K, this technique yields an estimated critical temperature of 420.3 K.

The third method that was examined was to determine the Lyderson structural contribution for the chlorine atom from experimental data for ethane and ethyl chloride. This method led to an estimate of 424.2 K. A value of 425 K was selected for the critical temperature with an estimated uncertainty of ±5 K. This estimation agrees (exactly) with the value estimated by Ambrose in his vapor pressure correlation but is slightly lower than that used previously by Reid et al. (*11*).

Similar procedures for the critical volume, V_c, and critical pressure, P_c, led to estimates of 187 ± 3 cm^3/mol and 5540 ± 200 kPa, respectively. The critical pressure estimate differs somewhat from that used by Ambrose (*14*); however, this difference would not affect results, since the vapor pressure correlation is formulated on a reduced basis. Table III summarizes the estimated critical constants and other fixed point constants for VCM that were used in this work.

Table III. Summary of Property Data for Vinyl Chloride

property	value	uncertainty
mol wt	62.499	
normal bp, K	259.43	0.5
critical temp, K	425.0	5.0
critical press., kPa	5540.0	200.0
critical vol, cm^3/mol	178.0	3.0
acentric factor	0.157	0.02

Effect of Pressure on the Liquid Density. As mentioned previously, no experimental measurements of the density of compressed liquid VCM have been reported previously in the chemical literature. For this reason, the effect of pressure on the saturated liquid density was estimated by using an extension of the principle of corresponding states due to Leland (*17*, *18*), Rowlinson (*19*), and their co-workers. In this model, two pure substances are defined to be in corresponding states by the following two equations:

$$Z_\alpha(P,T) = Z_0(h_{\alpha,0}P/f_{\alpha,0}; T/f_{\alpha,0})$$

$$G_\alpha^*(P,T) = f_{\alpha,0}G_0^*(h_{\alpha,0}P/f_{\alpha,0}; T/f_{\alpha,0})$$

In these equations the subscript α denotes the fluid of interest (VCM in our case) and the subscript 0 denotes the reference fluid for which we know the thermodynamic properties. In our work with VCM, we have chosen ethylene as the reference fluid. Z and G^* represent the compressibility factor, PV/RT, and residual Gibbs free energy, respectively. The factors $f_{\alpha,0}$ and $h_{\alpha,0}$ are slowly varying functions of temperature and density which are always close to the ratios of the critical temperatures and critical volumes, respectively, of the fluid α and the reference fluid 0. They are normally expressed as

$$f_{\alpha,0} = (T_c^\alpha/T_c^0)\theta_{\alpha,0}(\rho,T) \tag{10}$$

$$h_{\alpha,0} = (V_c^\alpha/V_c^0)\phi_{\alpha,0}(\rho,T) \tag{11}$$

where the functions $\theta_{\alpha,0}$ and $\phi_{\alpha,0}$ are called shape factors.

The key to success in the application of this method lies in the determination of the shape factors. In Leland's work a generalized correlation for the shape factors in terms of the reduced temperature, volume, and Pitzer's acentric factor was recommended. This generalization, which was based on hydrocarbons with methane as a reference fluid, is not applicable to VCM because of the chemical nature of this compound. Because of this, a new method of determining the shape factors was developed. In this method it is assumed that the shape factors for the liquid are effectively independent of the pressure in the range of 10–7000 kPa. Thus, the shape factors can be determined by the simultaneous solution of the appropriate extended corresponding states equations for the saturated liquid density and vapor pressure, viz.

$$P_\sigma^0(T_\sigma/f_{\alpha,0}) = h_{\alpha,0}P_\sigma^\alpha(T_\sigma)/f_{\alpha,0}$$

$$\rho_\sigma^0(T_\sigma/f_{\alpha,0}) = h_{\alpha,0}\rho_\sigma^\alpha(T_\sigma)$$

Combining these equations, we find

$$P_\sigma^0(T_\sigma/f_{\alpha,0}) = [\rho_\sigma^0(T_\sigma/f_{\alpha,0})/\rho_\sigma^\alpha(T_\sigma)]P_\sigma^\alpha(T_\sigma)/f_{\alpha,0} \tag{12}$$

which can be solved numerically for any value of T_σ. The correlations for VCM (α) used in this solution were presented earlier. For the reference fluid (0), Goodwin's nonanalytic equation of state (*20*, *21*) for ethylene was used.

Goodwin's Equation of State for Ethylene. Goodwin's equation of state (*20*) is specifically structured to be consistent with the known behavior of specific heats over the entire domain of fluid states. It originates on the liquid–vapor coexistence boundary, which is described by equations for the vapor pressure and orthobaric densities. The mathematical form of the equation is

$$P = P_\sigma[T_\sigma(\rho)] + \rho R[T - T_\sigma(\rho)] + \rho^2(RT_c/P_c)F(\rho,T)$$

where

$$F(\rho,T) = B(\rho)\,\Phi(\rho,T) + E(\rho)\,\Psi(\rho,T)$$

The functions $B(\rho)$, $\Phi(\rho,T)$, $E(\rho)$, and $\Psi(\rho,T)$ are defined as follows:

$$B(\rho) = b_1 + b_2\rho^* + b_3\rho^{*2}$$

$$\Phi(\rho) = T^{*\beta}\exp\{b_0[1 - T_\sigma(\rho)/T]\} - T_\sigma^{*\beta}$$

$$E(\rho) = E_1(\rho^* - 1)(\rho^* - E_r)\exp[-\gamma\rho^{*2}]$$

$$\Psi(\rho,T) = \delta\exp[\epsilon(1 - T^*)] + (1 - \delta)[1 - \omega + \omega\ln\omega] - \delta\exp[\epsilon(1 - T_\sigma^*)] + (1 - \delta)[1 - \omega_\sigma + \omega_\sigma\ln\omega_\sigma]$$

In these equations $T_\sigma(\rho)$ is the saturation temperature corresponding to the density, ρ, R is the gas constant, P is the absolute pressure, T is the absolute temperature, and ω is defined as

$$\omega(\rho,T) = 1 - \theta(\rho)/T$$

where

$$\theta = T_\sigma(\rho)\exp[-\alpha|(\rho^* - 1)^3/(\rho_t^* - 1)^3|]$$

A starred (*) quantity indicates a variable reduced by the value of the corresponding quantity at the critical point, the subscript t refers to the triple point, and the subscript σ refers to the orthobaric (saturation) boundary. The 11 equation of state parameters b_0–b_3, E_1, E_r, α, β, γ, δ, and ϵ were determined by fitting experimental data (see ref *15*).

Since at saturation the equation of state reduces to the identity $P = P_\sigma$, a separate representation of the orthobaric densities and vapor pressures is required. Goodwin's model uses the following correlations:

vapor pressure

$$\ln[(P_\sigma(T)/P_\sigma(T_t)] = a_0u + \sum_{i=1}^{3} a_ix_t^i + a_1x_t(1 - x_t)^\epsilon \quad (13)$$

saturated liquid density

$$\rho_{\sigma,l}^* = 1 + a_0x_c^{\epsilon'} + \sum_{n=1}^{4} a_nx_c^{(n+2)/3} \quad (14)$$

saturated vapor density

$$\rho_{\sigma,v}^* = \frac{RT_\sigma}{p_\sigma(T)}\left[1 + (Z_c - 1)\frac{P_\sigma^*}{T_\sigma^{*2}}f(T_\sigma^*)\right]^{-1} \quad (15)$$

where

$$f(T_\sigma^*) = 1 + a_0(1 - T_\sigma^*)^{\epsilon'} + \sum_{n=1} a_n(1 - T_\sigma^*)^n$$

In these equations $x_t = (T - T_t)/(T_c - T_t)$, $u = x_t/T_\sigma^*$, and $x_c = (T_c - T)/(T_c - T_t)$.

Shape Factors Evaluation and Corresponding States Calculation. The shape factors θ and ϕ which appear in eq 10 and 11 are obtained by simultaneously solving eq 8, 9, 13, and 14. Table IV lists the shape factors as a function of temperature that were determined by this procedure.

Once the shape factors were determined, Goodwin's equation of state was used to calculate the effect of pressure on the liquid vinyl chloride density using the following equation:

$$\rho^\alpha(T,P) = \rho^0(T/f_{\alpha,0},h_{\alpha,0}P/f_{\alpha,0})/h_{\alpha,0}$$

Table IV. Shape Factors at Several Temperatures for Saturated Liquid Vinyl Chloride (α) with Respect to Ethylene (0)

T, K	$\theta_{\alpha,0}$	$\phi_{\alpha,0}$	T, K	$\theta_{\alpha,0}$	$\phi_{\alpha,0}$
277.594	1.031 06	0.971 136	333.150	1.020 66	0.977 640
288.705	1.028 87	0.972 377	344.261	1.018 71	0.978 944
299.817	1.026 75	0.973 664	355.372	1.016 77	0.980 212
310.928	1.024 67	0.974 982	366.483	1.014 85	0.981 441
322.039	1.022 64	0.976 313			

As was mentioned previously, the assumption was made in these calculations that the shape factors were effectively independent of pressure in the region of interest. Calculations with Leland's generalized shape factor formula showed this to be valid to within ±0.01% which contributes to, but is 1 order of magnitude less than, the estimated uncertainty in these calculations. The densities predicted by the corresponding states calculations agree with the experimental densities with an average absolute deviation of 0.02%, with the largest deviation between a predicted density and a calculated density being 0.06%.

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Glossary

A, B, C, ...	various correlation parameters
F	densimeter period of oscillation
G	Gibbs free energy
k	densimeter k factor
T	absolute temperature
V	volume
a, b, c, ...	various correlation parameters
f, h	extended corresponding states parameters
P	absolute pressure
α, β, ...	various correlation parameters
θ, ϕ	extended corresponding states shape factors
ρ	density

Subscripts and Superscripts

c	liquid–vapor critical property
t	triple-point property
*	property reduced by its value at the critical point
0	reference fluid in corresponding states calculations
α	unknown fluid in corresponding states calculations
σ	orthobaric (saturation) boundary

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Isobaric Vapor–Liquid Equilibria of Toluene–Butyl Cellosolve Mixtures

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Isobaric vapor–liquid equilibria of the system toluene–butyl cellosolve at 760 ± 1 mmHg have been reported. This system exhibits positive deviations from Raoult's law. The vapor composition is predicted from experimental *t*–*x* data using the Wilson equation as well as UNIFAC parameters. The Wilson equation predicted the vapor composition well, whereas the UNIFAC method predicted the vapor composition with an average absolute error of 0.034 mole fraction.

Toluene is used as a diluent for butyl cellosolve in its application as an industrial solvent. The vapor–liquid equilibrium data for the system toluene–butyl cellosolve is of use in designing a solvent recovery system. So far the vapor–liquid equilibrium data of this system have not been reported. Hence, the vapor–liquid equilibrium data at 760 ± 1 mmHg pressure are determined and reported here.

Experimental Section

Materials. Analytical-grade toluene from the British Drug House Co. (India) is double distilled in a laboratory distillation column. Butyl cellosolve supplied by Naarden (Holland) is distilled under vacuum, and the middle fraction whose boiling point at atmospheric pressure coincides with that reported in the literature is collected and used. Table I compares the physical properties of the chemicals with the literature values.

Equilibrium Still. A vapor recirculating still of Jones as modified by Ward (*1*) is used to determine the vapor–liquid equilibrium compositions. A still with a total capacity of about 60 mL is used. The still and the experimental technique have been described elsewhere (*2*). When the equilibrium temperature is attained in the still, this temperature is maintained for 2 h to ensure equilibrium conditions. The equilibrium temperature is measured by using a standard mercury-in-glass thermometer having an accuracy of ±0.1 °C.

Analysis. The composition of the equilibrium samples is determined by refractive index. Refractive index measurements are taken at 30 ± 0.1 °C for sodium light with an Abbe precision refractometer capable of reading up to 0.0005. Water from a constant-temperature bath maintained at 30 ± 0.1 °C is circulated through the prism of the refractometer. The compositions in mole percent are determined from a standard plot of refractive index vs. composition prepared earlier by using mixtures of known composition. The maximum error in the composition measurement by refractive index is estimated to be ±0.007 mole fraction.

Results and Discussion

The vapor–liquid equilibrium data at 760 ± 1 mmHg pressure are presented in Table II.

The liquid-phase activity coefficient of each component is calculated from the expression

$$\gamma_i = \frac{\phi_i^{V}\pi y_i}{\phi_i^{S}P^\circ_i x_i[V_i^{L}(\pi - P^\circ_i)/RT]} \qquad (1)$$

The fugacity coefficients are calculated by using the virial equation truncated after the second term. The second virial coefficient and molar volume data are estimated from Hayden and O'Connel (*3*) and Yen and Woods (*4*) correlations, respectively. The Antoine constants (*5*) for toluene and butyl cellosolve are modified to fit the experimental boiling temperatures and are used to compute the vapor pressures.

From the activity coefficient data it is found that this system exhibits small positive deviation from Raoult's law.

The data are found to be consistent by the point-to-point method (*6*).

The Wilson equation (*7*) and the UNIFAC method are used to predict the vapor compositions from *t*–*x* data. As the fugacity coefficient ratio ϕ_i^{V}/ϕ_i^{S} and the Poynting factor in eq 1 are found to be around unity, these correction factors are neglected in the prediction of vapor composition by the two methods.

In the case of the Wilson equation, a nonlinear least-squares minimization procedure (*8*) which optimizes Wilson parameters while predicting the vapor compositions is used with the following objective function:

$$F = \sum_{1}^{N}[1 - (y_{1,\text{calcd}} + y_{2,\text{calcd}})]^2 \qquad (2)$$

The estimated vapor composition is presented in Table II. The

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