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Vapor–Liquid Equilibria of the Trimethyl Borate (1)–Trichloroethylene (2) System

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Vapor–liquid equilibria for the binary system trimethyl borate (1)–trichloroethylene (2) have been measured at 101.325 kPa. Data were shown to approach ideality and could also be reasonably represented by a constant relative volatility α_{12} = 1.782.

Isobaric vapor–liquid equilibria for the binary system trimethyl borate (1)–trichloroethylene (2) were measured at 101.325 ± 0.3 kPa (760 ± 2 mmHg) in an Altsheler circulation-type still. Details of the Altsheler still can be found in the paper by Altsheler et al. (*1*). The still contained two thermocouples, one submerged in the boiling liquid and one in the vapor space directly above the boiling liquid. The two copper–constantan thermocouples were tested external to the apparatus at the ice point and 298.15 K. The latter temperature was established by using an NBS thermometer certified to ±0.05 K. The thermocouples were also tested in place while boiling distilled water at 760 ± 2 mm Hg. These tests in comparison with standard thermocouple emf tables indicated a potentiometer–thermocouple combination accuracy of ±(0.005 mV/0.0045 mV/K) or ±0.11 K over the range. At all times during boiling of pure components, both thermocouples indicated the same temperature; however, when the binary was investigated, the vapor thermocouple sometimes read higher. Maximum variation was +0.2 K. When variations occurred, the liquid temperature was reported. Temperatures are believed to be accurate to approximately ±0.1 K.

Materials Used

The trimethyl borate was manufactured by the Aldrich Chemical Co. and was received with a nominal purity of 99%. A portion was subjected to simple distillation, and no measurable change in boiling point or refractive index was found. Therefore, the borate was used with no additional purification. The trichloroethylene was purchased from Fisher Scientific Co. at 99.9% purity and was also used as received. Table I shows the properties of these material as compared with literature values.

Methods of Analysis

A Bausch & Lomb precision refractometer along with a carefully prepared calibration curve was used to determine composition of the liquid and condensed vapor phases. The refractometer used a sodium D line as the light source and provided a precision ±0.000 03 RI unit. The prism in the refractometer was maintained at a temperature of 298.15 ± 0.1 K. The calibration curve was established with 20 samples prepared by gravimetric measurements (±0.000 05 g). Reproducibility of these and samples taken from the Altsheler still was at least within ±0.0005 mole fraction.

Table I. Physical Properties of the Pure Components

Trimethyl Borate	
boiling point, K (760 mmHg)	
lit.	340.15–342.15 (*2*) 341.62 (*3*)
measd	341.99
refractive index (298.15 K)	
lit.	1.354 41 (*3*)
measd	1.354 48
Trichloroethylene	
boiling point, K (760 mmHg)	
lit.	360.15 (*4*)
measd	360.55
refractive index	
lit.	1.477 3 (293.15 K) (*2*)
measd	1.474 18 (298.15 K)

Vapor Pressure Equations

trimethyl borate (*5*)
$\ln P^\circ = 13.1756 - 1357.14/(T - 134.33)$
trichloroethylene (*4*)
$\ln P^\circ = 16.1827 - 3028.13/(T - 43.15)$

Discussion of Results

Activity coefficients were calculated from the experimental data by using the equation

$$\gamma_i = \frac{y_i \pi}{\Phi\, x_i\, P_i^\circ} \qquad (1)$$

where

$$\Phi = \phi_i \exp\left[\frac{1}{RT}\int_{P_i^\circ}^{\pi} v_i d\right] \Big/ \hat{\phi}_i \qquad (2)$$

and Φ, the "correction factor", is the ratio of the fugacity coefficient of the pure component at its vapor pressure to the component in the vapor mixture at the total pressure, multiplied by the Poynting correction. Fugacity coefficients were calculated by the Redlich–Kwong–Soave equation. Values of Φ ranged from 0.99 to 1.02. Values of the activity coefficient calculated in this manner showed a scattering around the value of unity with a maximum deviation of approximately −0.04. The average deviation of γ_1 and γ_2 was ±0.014. Because of these

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Table II. Experimental Results

	borate mole fraction			
T ±0.1, K	x	y	y^a	T,[b] K
360.6	0.000	0.000	0.000	360.7
359.8	0.028	0.047	0.047	359.6
359.2	0.051	0.081	0.084	359.1
358.7	0.067	0.110	0.110	358.7
358.5	0.074	0.119	0.121	358.5
357.9	0.103	0.163	0.165	357.9
357.0	0.142	0.227	0.223	357.0
356.5	0.162	0.255	0.251	356.6
355.5	0.211	0.316	0.317	355.5
354.8	0.245	0.357	0.361	354.8
353.5	0.296	0.426	0.423	353.7
353.2	0.312	0.450	0.442	353.4
352.6	0.349	0.487	0.484	352.7
352.0	0.385	0.522	0.523	352.0
351.6	0.411	0.552	0.551	351.5
350.5	0.457	0.599	0.597	350.6
350.1	0.482	0.625	0.622	350.2
349.2	0.526	0.666	0.663	349.3
348.6	0.572	0.709	0.703	348.5
348.1	0.601	0.733	0.728	348.0
347.5	0.626	0.750	0.749	347.6
346.9	0.675	0.789	0.787	346.8
345.9	0.734	0.832	0.831	345.8
345.2	0.785	0.870	0.867	345.0
345.1	0.795	0.877	0.874	344.9
343.4	0.870	0.927	0.923	343.6
343.3	0.902	0.943	0.943	343.2
343.0	0.919	0.955	0.953	342.9
342.6	0.950	0.974	0.972	342.5
342.0	1.000	1.000	1.000	341.8

[a] Values calculated assuming eq 3. [b] Iterated temperatures.

calculated small and random deviations from ideality, the data were also examined by using the ideal system representation

$$y_i = x_i P_i^\circ / \pi \qquad (3)$$

Values of y were estimated at measured values of x using temperature iterations until the sum of the y values equaled unity. The experimental T-x-y data as well as the estimated data are shown in Table II. The average deviation is less than 0.003 mole fraction. The iterated ideal system temperatures, for the large majority of the points, converged to within ±0.1 K or the accuracy of the experimental measurements. This along with possible errors in data (total measured pressure, vapor-phase estimations, and vapor pressure equations) necessary to evaluate activity coefficients leads to the conclusion that the system closely approximates ideality within the accuracy of the data available. Figure 1 compares the estimated data with the experimental data. The lower portion of the figure shows the deviation of each point.

The data may also be reasonably represented by the constant relative volatility equation

$$y_1 = \frac{\alpha_{12} x_1}{1 + (\alpha_{12} - 1) x_1} \qquad (4)$$

with α_{12} = 1.782. This yields an averge error in y slightly greater than 0.003.

Glossary

P°	vapor pressure, mmHg
R	gas constant
T	temperature, K
v_i	liquid volume
x	liquid-phase composition, mole fraction
y	vapor-phase composition, mole fraction

Greek Letters

α	relative volatility
γ	activity coefficient
π	total pressure
Φ	correction factor defined by eq 2
$\hat{\phi}_i$	fugacity coefficient in vapor mixture at total pressure
ϕ_i	fugacity coefficient of pure gaseous component at P°

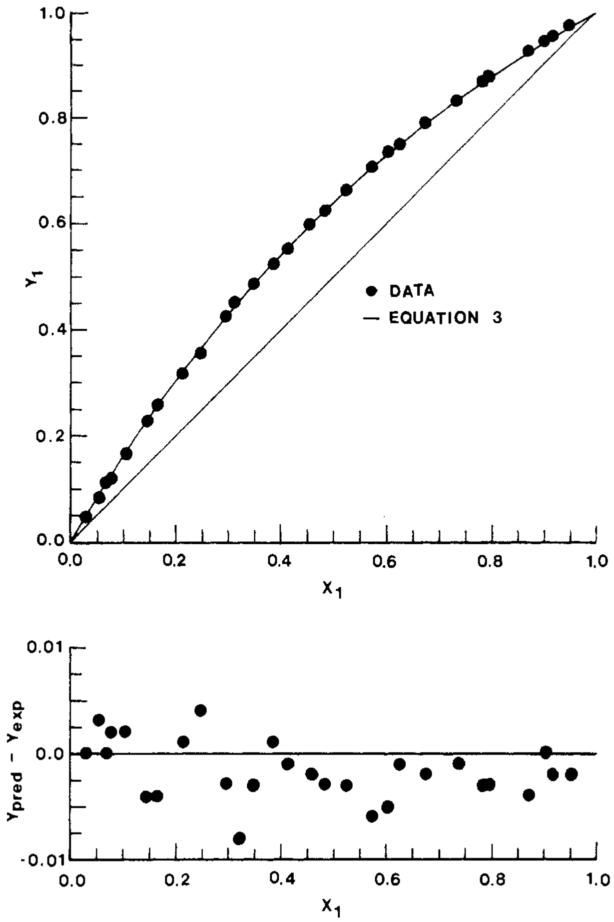

Figure 1.

Registry No. $B(OMe)_3$, 121-43-7; C_2HCl_3, 79-01-6.

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