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Supplementary Material Available: All of our experimental density, viscosity, and vapor pressure data (2 pages). Ordering information is given on any current masthead.

Vapor-Liquid Equilibria of the System Trimethyl Borate (1)-*n*-Cyclohexane (2)

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Vapor-liquid equilibria for the binary system trimethyl borate (1)-*n*-cyclohexane (2) have been measured at 101.325 kPa. The data have been checked for thermodynamic consistency and also correlated by the Wilson equations.

Isobaric vapor-liquid equilibrium data for the system trimethyl borate (1)-*n*-cyclohexane (2) were measured at 101.325 kPa \pm 0.3 (760 \pm 2 mmHg) in an Altsheler circulation-type still. Details of the Altsheler still can be found in the reference by Hala 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 thermocouples were calibrated; however, they did not always give the same value during still operation. Maximum variation was \pm 0.3 K. When variations occurred, the liquid temperature was reported. Temperatures are believed to be accurate to \pm 0.1 K.

Materials Used

The trimethyl borate was manufactured by the Aldrich Chemical Co. and was received with a nominal purity of 99%. This purity was not sufficient, so the chemical was further purified by simple distillation. The *n*-cyclohexane was manufactured by Burdick & Jackson and was received with a purity of 99.9%. The purity was acceptable and the *n*-cyclohexane was used as received. Properties of these materials compared with literature values are shown in Table I.

Methods of Analysis

A Bausch & Lomb precision refractometer along with a carefully prepared calibration curve was used to determine composition of the liquid phase and the vapor phase. The refractometer used a sodium D-line as the light source and provided a precision of \pm 0.000 03 RI units. The prism in the refractometer was maintained at a temperature of 298.15 \pm 0.1 K.

Discussion of Results

The experimental results are shown in Table II and Figure 1. Data show that the system exhibits positive deviations from Raoult's law and does not possess an azeotrope. The activity

Table I. Physical Properties of the Pure Components

Trimethyl Borate	
boiling point, K	
lit.	341.85 (2)
measd	341.62
refractive index (temp, K)	
lit.	1.35422 (300.15) (3)
	1.35503 (298.15) (3)
	1.3550 (298.15) (4)
	1.35517 (298.15) (5)
measd	1.35441 (298.15)
<i>n</i> -Cyclohexane	
boiling point, K	
lit.	353.87 (6)
	353.85 (7)
measd	353.88
refractive index (temp, K)	
lit.	1.4262 (293.15) (6)
	1.4266 (293.15) (7)
measd	1.4275 (298.15)
	1.4264 (293.15)
Vapor Pressure Equations	
trimethyl borate (8)	
	$\ln P^0 = 13.1756 - 1357.14/(T - 134.33)$
<i>n</i> -cyclohexane (9)	
	$\ln P^0 = 15.7527 - 2766.63/(T - 50.50)$

coefficients range between 1.000 and the estimated infinitely dilute values of $\gamma_1^\infty = 1.563$ and $\gamma_2^\infty = 1.408$. All of the activity coefficients except for the infinite dilution values were calculated by the equation

$$\gamma_i = y_i \pi / \Phi x_i P^0$$

where

$$\Phi = \phi_i \exp \left[\frac{1}{RT} \int_{P^0}^{\pi} V_i d\pi \right] / \hat{\phi}_i$$

and 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 exponential term called the Poynting correction. Fugacity coefficients were calculated by using the Redlich and Kwong equation of state. Values of Φ ranged from 0.98 to 1.02.

The data were subjected to a thermodynamic consistency test as suggested by Fredenslund et al. (10). In this procedure the excess Gibbs function is expressed as a Legendre poly-

Table II. Experimental Results

$T \pm 0.1, \text{K}$	(borate) mole fractn		activity coeff		G^E/RT^a
	liquid x_1	vapor y_1	γ_1	γ_2	
353.9	0.000	0.000		1.000	0.0000
353.4	0.014	0.028	1.481	1.001	0.0060
352.3	0.039	0.079	1.523	1.035	0.0442
351.7	0.061	0.120	1.492	1.005	0.0203
351.4	0.066	0.127	1.468	1.006	0.0307
350.0	0.113	0.197	1.375	1.014	0.0478
350.2	0.113	0.200	1.387	1.005	0.0414
349.6	0.130	0.225	1.375	1.012	0.0518
348.7	0.167	0.278	1.359	1.009	0.0585
347.8	0.207	0.323	1.310	1.023	0.0740
347.3	0.261	0.373	1.211	1.031	0.0726
346.9	0.281	0.393	1.203	1.040	0.0802
346.4	0.299	0.418	1.214	1.038	0.0841
346.3	0.321	0.434	1.182	1.043	0.0825
345.9	0.348	0.458	1.167	1.055	0.0884
345.8	0.354	0.455	1.140	1.074	0.0929
345.6	0.381	0.492	1.153	1.054	0.0866
345.3	0.399	0.507	1.142	1.060	0.0879
345.2	0.424	0.525	1.121	1.070	0.0872
344.7	0.431	0.533	1.132	1.081	0.0974
344.2	0.476	0.571	1.115	1.096	0.0996
344.2	0.508	0.591	1.084	1.113	0.0935
343.3	0.591	0.660	1.066	1.148	0.0943
342.8	0.662	0.715	1.045	1.180	0.0850
342.7	0.721	0.764	1.030	1.188	0.0692
342.4	0.751	0.786	1.027	1.213	0.0681
342.2	0.758	0.790	1.030	1.237	0.0736
342.1	0.865	0.879	1.006	1.289	0.0396
342.1	0.870	0.884	1.008	1.271	0.0384
342.0	0.873	0.888	1.011	1.270	0.0402
341.8	0.883	0.900	1.018	1.232	0.0399
341.7	0.909	0.921	1.015	1.261	0.0344
341.6	1.000	1.000	1.000		0.0000

^a Excess Gibbs function.

mial (second order in this study) and set equal to the experimental values of the excess Gibbs function. The polynomial representation enables the calculation of a correlated set of activity coefficients by making use of the partial molal relationship to the excess function. When the activity coefficients are known, vapor-phase mole fractions are calculated and compared to the experimental values. In this study the average deviation between measured and estimated vapor concentrations was 0.005 mole fraction.

The data were then correlated to the Van Laar, Margules, and Wilson models (11). The best overall fit of the data was by the Wilson model with temperature-independent parameters $G_{12} = 0.608$ and $G_{21} = 1.051$. The average error in vapor-phase compositions by this model was less than 0.004 mole fraction. The line in the upper part of Figure 1 represents this Wilson model and the lower part shows the deviation of each point.

Glossary

G^E	excess Gibbs function
G_{ij}^E	binary parameter for Wilson equations
P^0	vapor pressure, mmHg
R	gas constant
T	temperature, K
V	volume
x	liquid-phase composition, mole fraction
y	vapor-phase composition, mole fraction

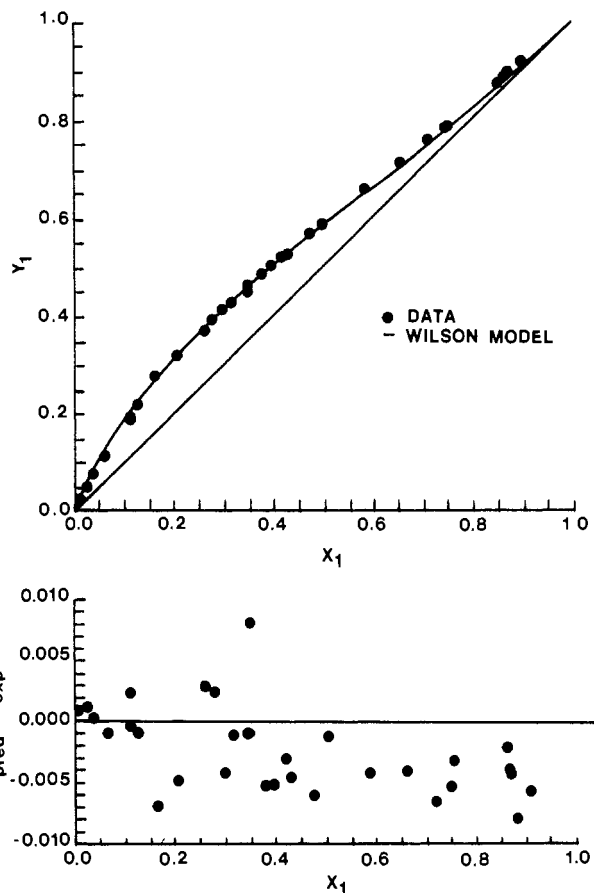


Figure 1. Comparison of the Wilson model to the experimental equilibrium data for the system trimethyl borate(1)-*n*-cyclohexane (2).

Greek Letters

γ	activity coefficient
π	total pressure, mmHg
Φ	ratio of fugacity coefficients multiplied by the Poynting correction
$\hat{\phi}$	fugacity coefficient in vapor mixture at total pressure
ϕ	fugacity coefficient of pure component at P^0

Registry No. Trimethyl borate, 121-43-7; *n*-cyclohexane, 110-82-7.

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