Subscripts

1, 2 components

Registry No. MeOH, 67-56-1; EtOH, 64-17-5; $(MeO)_4Si$, 681-84-5; $(EtO)_4Si$, 78-10-4.

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Vapor–Liquid Equilibrium of 1,3-Dioxolane Systems

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We report here the vapor–liquid equilibrium of 1,3-dioxolane and of binary mixtures of 1,3-dioxolane separately with cyclohexane at 313.15 and 333.15 K, with heptane at 313.15 and 343.15 K, with water at 318.15 and 343.15 K, with ethanol at 313.15 and 338.15 K, and with chloroform at 308.15 and 323.15 K. These data are correlated with five liquid activity coefficient models using the maximum likelihood parameter estimation method with a correlation for nonideal vapor-phase behavior.

Introduction

Cyclic ethers are frequently used as solvents in chemical industry because of their unique physicochemical nature. Tetrahydrofuran has a single cyclic ether group, 1,4-dioxane has two cyclic ether groups separated by two methylene groups, while 1,3-dioxolane has two cyclic ether groups separated by one methylene group. Vapor–liquid equilibrium (VLE) data have already been published for mixtures of tetrahydrofuran (*1*, *2*) and of 1,4-dioxane (*3*) with alkanes, water, and chloroform. We measured VLE of mixtures containing 1,3-dioxolane in order to obtain liquid activity coefficients for these mixtures which is of inherent interest and also of use in testing proximity effects in current group contribution activity coefficient models (which will be done elsewhere.) Five binary mixtures were measured, each at two isotherms: the VLE of 1,3-dioxolane with cyclohexane at 313.15 and 333.15 K, with heptane at 313.15 and 343.15 K, with water at 318.15 and 343.15 K, with ethanol at 313.15 and 338.15 K, and with chloroform at 308.15 and 323.15 K.

Experiments

The experimental equipment and operating procedures have been described in detail previously (*4*). The VLE measurements were done with a Stage-Muller dynamic still. The temperature was measured with a platinum resistance thermometer (Rosemount Model 162N) accurate to 0.02 K with a resolution of 0.001 K. Pressures were measured with an accuracy of 0.02 kPa by using a Wallace-Tiernan Model FA-187 precision mercury manometer. Vapor and liquid equilibrium samples were analyzed by using a Hewlett-Packard Model 5730 gas chromatograph with a Model 3390 integrator, after calibration with gravimetrically prepared samples. The compositions determined in this way are accurate to better than 0.005 in mole fraction.

Table I. Pure Component Vapor Pressure of 1,3-Dioxolane ($C_3H_6O_2$)

temp, K	press., kPa	temp, K	press., kPa
304.443	18.018	329.590	51.609
304.460	18.025	333.294	59.328
308.195	21.373	337.050	68.052
313.343	26.793	340.606	77.295
317.920	32.478	343.290	84.772
321.450	37.525	347.540	97.959
325.525	44.144		

Table II. Antoine Constants Used in This Work

$$\log P(\mathrm{kPa}) = A - \frac{B}{T(^\circ\mathrm{C}) + C}$$

component	A	B	C	temp range, °C
1,3-dioxolane	6.23182	1236.70	217.235	30–75
cyclohexane	6.15159	1301.67	233.445	20–80
heptane	5.90871	1196.68	208.230	20–100
water	7.21358	1739.35	234.100	40–49
water	7.10946	1678.948	228.970	70–79
ethanol	7.16879	1552.60	222.419	30–78
chloroform	5.96288	1106.94	218.552	30–60

In this study 1,3-dioxolane, cyclohexane, heptane, and chloroform were of Gold Label quality from Aldrich Chemical Co. and were used as received. The water used was filtered, distilled, and deionized. Ethanol is 200-proof dehydrated alcohol from U.S. Industrial Chemicals Corp. The vapor pressures of cyclohexane, heptane, chloroform, water, and ethanol agree to within 0.1 kPa with literature values (*5*). The vapor pressure of 1,3-dioxolane that we measured is slightly different from the one data set reported (*5*). However, our measured vapor pressure data for 1,3-dioxolane, listed in Table I, are not only better fit with the Antoine equation than the other measurements, but also are in better agreement with the reported normal boiling point (*6*). Consequently, we believe our measurements to be of high accuracy. The Antoine constants that we determined from our vapor pressure measurements are listed in Table II. The binary isothermal VLE data we measured are listed in Table III. These data satisfy thermodynamic consistency tests (*7*).

Results and Discussion

We correlated our measured vapor–liquid equilibrium data with five liquid activity coefficient models using the maximum likelihood parameter estimation method, with a nonideal vapor phase correction using second virial coefficients obtained from the correlation of Hayden and O'Connell (*8*). The second virial coefficients we used are listed in Table IV. The experimental

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Table III. Experimental Vapor-Liquid Equilibria[a]

P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1
			1,3-Dioxolane (1)/Cyclohexane (2) at 313.15 K					
24.617	0.0000	0.0000	37.165	0.4550	0.5144	32.095	0.9275	0.7867
25.345	0.0066	0.0309	37.274	0.5365	0.5397	29.955	0.9623	0.8669
27.581	0.0347	0.1325	37.147	0.6325	0.5698	28.108	0.9859	0.9433
30.816	0.0862	0.2551	36.985	0.6737	0.5845	27.055	0.9965	0.9783
33.792	0.1660	0.3601	36.400	0.7609	0.6223	26.555	1.0000	1.0000
35.788	0.2649	0.4336	35.485	0.8200	0.6624			
36.740	0.3646	0.4821	34.038	0.8792	0.7160			
			1,3-Dioxolane (1)/Cyclohexane (2) at 333.15 K					
51.961	0.0000	0.0000	77.172	0.4357	0.5165	68.705	0.9228	0.8065
53.455	0.0098	0.0373	77.705	0.5255	0.5502	64.832	0.9608	0.8850
57.070	0.0333	0.1133	77.698	0.6064	0.5811	61.541	0.9850	0.9497
63.555	0.0889	0.2455	77.222	0.6822	0.6124	60.120	0.9935	0.9777
69.187	0.1563	0.3427	76.098	0.7591	0.6510	59.016	1.0000	1.0000
73.488	0.2526	0.4200	74.231	0.8286	0.6969			
75.940	0.3472	0.4757	71.602	0.8826	0.7509			
			1,3-Dioxolane (1)/Heptane (2) at 313.15 K					
12.242	0.0000	0.0000	29.162	0.4400	0.6738	30.330	0.7603	0.7580
19.750	0.0748	0.4022	29.515	0.4961	0.6873	30.290	0.8169	0.7788
23.195	0.1348	0.5268	29.722	0.5209	0.6970	29.940	0.8977	0.8264
26.089	0.2315	0.6017	29.921	0.5633	0.7040	29.275	0.9373	0.8668
26.618	0.2426	0.6090	30.135	0.6266	0.7188	27.500	0.9857	0.9589
27.880	0.3060	0.6415	30.122	0.6320	0.7203	26.891	0.9951	0.9838
28.157	0.3400	0.6537	30.250	0.6961	0.7325	26.555	1.0000	1.0000
28.963	0.4007	0.6652	30.291	0.7275	0.7501			
			1,3-Dioxolane (1)/Heptane (2) at 343.15 K					
40.520	0.0000	0.0000	85.555	0.4065	0.6607	92.865	0.8287	0.8081
42.700	0.0103	0.0560	86.070	0.4183	0.6680	92.173	0.8821	0.8392
60.430	0.1066	0.3812	88.700	0.4983	0.6962	90.790	0.9258	0.8777
65.458	0.1448	0.4473	90.493	0.5731	0.7204	88.690	0.9611	0.9223
68.870	0.1753	0.4918	91.562	0.6332	0.7383	86.618	0.9829	0.9602
73.805	0.2231	0.5408	92.342	0.6820	0.7529	85.012	0.9955	0.9890
82.250	0.3407	0.6293	92.880	0.7609	0.7803	84.387	1.0000	1.0000
			1,3-Dioxolane (1)/Water (2) at 318.15 K					
9.585	0.0000	0.0000	32.110	0.1242	0.7220	36.100	0.8334	0.8103
9.621	0.0001	0.0062	33.750	0.1783	0.7360	35.874	0.8817	0.8341
9.890	0.0007	0.0251	34.548	0.2397	0.7502	35.634	0.9047	0.8572
14.750	0.0116	0.3527	34.935	0.3196	0.7530	35.389	0.9273	0.8766
17.750	0.0183	0.4496	35.252	0.4139	0.7522	34.709	0.9559	0.9122
22.120	0.0316	0.5559	35.553	0.5354	0.7613	32.795	1.0000	1.0000
29.240	0.0791	0.6739	35.894	0.6473	0.7644			
32.100	0.1204	0.7203	36.090	0.7637	0.7888			
			1,3-Dioxolane (1)/Water (2) at 343.15 K					
31.166	0.0000	0.0000	77.911	0.0941	0.6198	94.858	0.7809	0.7543
32.400	0.0009	0.0188	80.402	0.1008	0.6338	94.425	0.8338	0.7781
35.080	0.0024	0.0557	85.080	0.1468	0.6628	90.985	0.9375	0.8751
38.890	0.0063	0.1443	87.955	0.1891	0.6786	88.430	0.9630	0.9238
43.810	0.0101	0.2136	89.878	0.2369	0.6803	86.167	0.9845	0.9674
49.870	0.0145	0.3015	92.962	0.4029	0.6989	85.535	0.9885	0.9759
58.190	0.0205	0.4257	93.560	0.4609	0.7034	85.030	0.9915	0.9836
67.520	0.0406	0.5088	94.285	0.5306	0.7132	84.387	1.0000	1.0000
71.480	0.0542	0.5467	94.462	0.6066	0.7218			
72.550	0.0607	0.5576	94.942	0.7225	0.7369			
			1,3-Dioxolane (1)/Ethanol (2) at 313.15 K					
17.877	0.0000	0.0000	25.532	0.1520	0.3561	29.960	0.7901	0.7406
18.390	0.0058	0.0269	27.240	0.2309	0.4411	29.350	0.8680	0.8086
19.495	0.0201	0.0826	28.377	0.3079	0.4948	28.430	0.9318	0.8840
21.275	0.0468	0.1731	29.236	0.4017	0.5417	27.623	0.9684	0.9388
23.289	0.0837	0.2586	29.878	0.5172	0.5982	26.964	0.9870	0.9747
24.302	0.1123	0.3066	30.178	0.6136	0.6410	26.555	1.0000	1.0000
23.420	0.0889	0.2707	30.150	0.7015	0.6863			
			1,3-Dioxolane (1)/Ethanol (2) at 338.15 K					
58.468	0.0000	0.0000	78.003	0.2618	0.3960	78.110	0.8736	0.8067
59.768	0.0106	0.0348	80.038	0.3349	0.4468	75.319	0.9327	0.8819
61.570	0.0226	0.0695	81.391	0.4093	0.4886	72.870	0.9719	0.9466
64.070	0.0419	0.1193	82.651	0.5606	0.5732	71.382	0.9902	0.9810
68.260	0.0847	0.2014	82.539	0.6404	0.6173	70.795	1.0000	1.0000
72.085	0.1356	0.2734	81.843	0.7228	0.6707			
75.410	0.1959	0.3386	80.386	0.8007	0.7325			

Table III (Continued)

P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1
			1,3-Dioxolane (1)/Chloroform (2) at 308.15 K					
39.544	0.0000	0.0000	27.241	0.3799	0.2364	21.545	0.8872	0.8799
39.373	0.0067	0.0022	25.082	0.4684	0.3386	21.461	0.9354	0.9330
38.635	0.0304	0.0067	23.710	0.5540	0.4526	21.440	0.9724	0.9718
37.155	0.0759	0.0198	23.164	0.6125	0.5322	21.393	0.9929	0.9919
35.021	0.1373	0.0439	22.320	0.6897	0.6375	21.323	1.0000	1.0000
32.496	0.2131	0.0836	21.912	0.7601	0.7303			
29.775	0.2914	0.1457	21.648	0.8273	0.8106			
			1,3-Dioxolane (1)/Chloroform (2) at 323.15 K					
69.261	0.0000	0.0000	49.508	0.3832	0.2485	40.152	0.8876	0.8834
68.700	0.0100	0.0022	46.425	0.4677	0.3499	40.125	0.9377	0.9363
67.449	0.0344	0.0094	44.100	0.5544	0.4610	40.115	0.9727	0.9722
65.074	0.0797	0.0251	42.957	0.6100	0.5365	40.110	0.9919	0.9911
61.570	0.1424	0.0542	41.775	0.6901	0.6421	40.110	1.0000	1.0000
57.511	0.2161	0.0992	41.032	0.7568	0.7271			
53.280	0.2982	0.1631	40.593	0.8251	0.8098			

[a] x_1, liquid mole fraction; y_1, vapor mole fraction.

Table IV. Second Virial Coefficients and Liquid Molar Volumes[a]

component	temp, K	V	B_{ii}	B_{12}
1,3-dioxolane (i = 1)	308.15	79.04	−2046	
	313.15	79.50	−1907	
	318.15	79.97	−1782	
	323.15	80.44	−1670	
	333.15	81.43	−1478	
	338.15	81.94	−1395	
	343.15	82.46	−1320	
cyclohexane (i = 2)	313.15	79.54	−1128	−1024
	333.15	81.62	−968	−872
heptane (i = 2)	313.15	153.33	−2485	−1597
	343.15	159.50	−1876	−1227
ethanol (i = 2)	313.15	59.18	−1652	−659
	338.15	61.35	−1121	−549
water (i = 2)	318.15	18.20	−1242	−294
	343.15	18.63	−757	−245
chloroform (i = 2)	308.15	82.06	−1474	−4405
	323.15	83.61	−1251	−2947

[a] V, liquid molar volume (cm^3/(g·mol)); B_{ii}, second virial coefficients (cm^3/(g·mol)) for pure components; B_{12}, cross second virial coefficients (cm^3/(g·mol)) estimated by the method of Hayden and O'Connell.

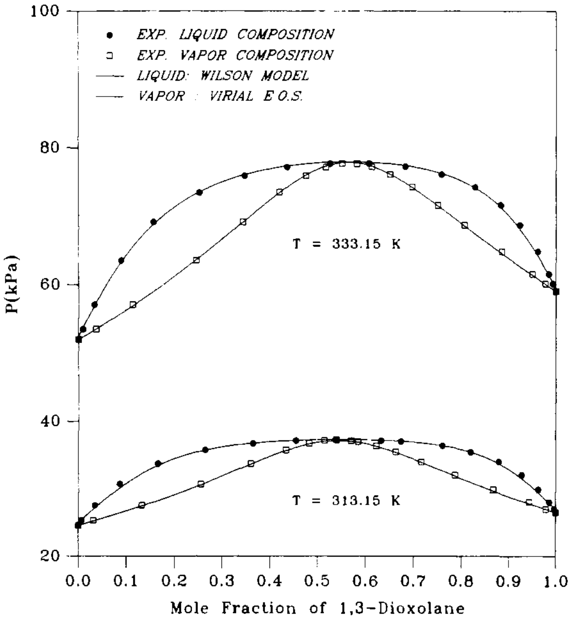

Figure 1. Vapor-liquid equilibrium of 1,3-dioxolane + cyclohexane at 313.15 and 333.15 K.

data together with the fit of the activity coefficient models which led to the best correlation are plotted in Figures 1-5. The

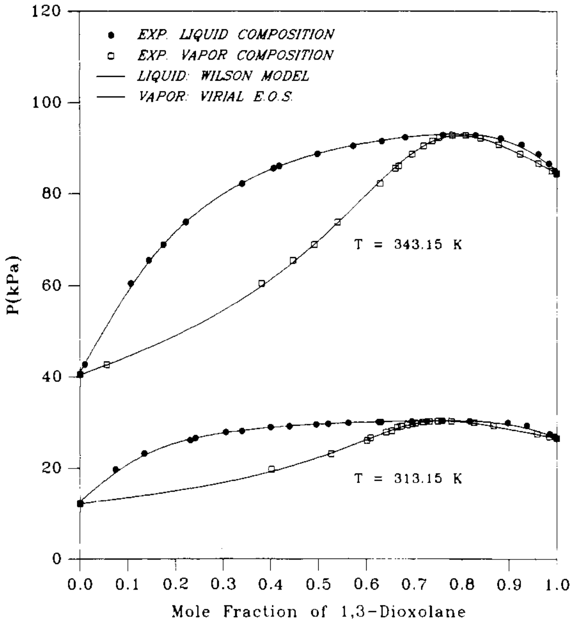

Figure 2. Vapor-liquid equilibrium of 1,3-dioxolane + heptane at 313.15 and 343.15 K.

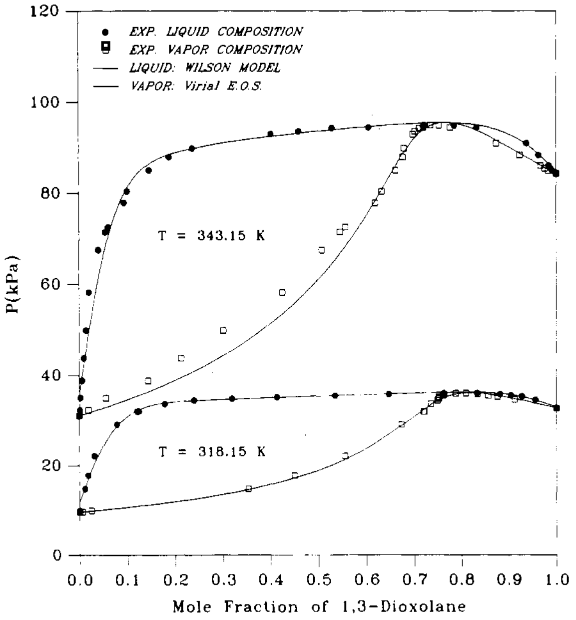

Figure 3. Vapor-liquid equilibrium of 1,3-dioxolane + water at 318.15 and 343.15 K.

Table V. Comparison of Liquid Activity Coefficient Models[a]

model	temp, K	δP, kPa	δy_1
1,3-Dioxolane (1) + Cyclohexane (2)			
Margules	313.15	0.190	0.0049
Van Laar	313.15	0.186	0.0047
Wilson	313.15	0.066	0.0027
NRTL	313.15	0.155	0.0042
UNIQUAC	313.15	0.172	0.0047
UNIFAC	313.15	9.25	0.1140
Margules	333.15	0.287	0.0030
Van Laar	333.15	0.277	0.0029
Wilson	333.15	0.125	0.0016
NRTL	333.15	0.240	0.0023
UNIQUAC	333.15	0.262	0.0026
UNIFAC	333.15	20.39	0.1192
1,3-Dioxolane (1) + Heptane (2)			
Margules	313.15	0.221	0.0078
Van Laar	313.15	0.209	0.0074
Wilson	313.15	0.112	0.0029
NRTL	313.15	0.182	0.0061
UNIQUAC	313.15	0.196	0.0069
UNIFAC	313.15	6.83	0.0735
Margules	343.15	0.474	0.0037
Van Laar	343.15	0.311	0.0023
Wilson	343.15	0.077	0.0022
NRTL	343.15	0.281	0.0022
UNIQUAC	343.15	0.407	0.0053
UNIFAC	343.15	22.01	0.0943
1,3-Dioxolane (1) + Water (2)			
Margules	318.15	1.117	0.0202
Van Laar	318.15	1.080	0.0191
Wilson	318.15	0.304	0.0120
NRTL	318.15	0.803	0.0129
UNIQUAC	318.15	0.483	0.0073
UNIFAC	318.15	11.86	0.2173
Margules	343.15	3.305	0.0187
Van Laar	343.15	3.147	0.0171
Wilson	343.15	0.818	0.0162
NRTL	343.15	2.671	0.0132
UNIQUAC	343.15	1.909	0.0092
UNIFAC	343.15	25.40	0.1836
1,3-Dioxolane (1) + Ethanol (2)			
Margules	313.15	0.149	0.0100
Van Laar	313.15	0.141	0.0100
Wilson	313.15	0.086	0.0096
NRTL	313.15	0.130	0.0099
UNIQUAC	313.15	0.130	0.0100
UNIFAC	313.15	1.52	0.0191
Margules	338.15	0.124	0.0026
Van Laar	338.15	0.116	0.0025
Wilson	338.15	0.209	0.0026
NRTL	338.15	0.244	0.0033
UNIQUAC	338.15	0.104	0.0023
UNIFAC	338.15	2.21	0.0125
1,3-Dioxolane (1) + Chloroform (2)			
Margules	308.15	0.100	0.0034
Van Laar	308.15	0.126	0.0042
Wilson	308.15	0.131	0.0042
NRTL	308.15	0.123	0.0040
UNIQUAC	308.15	0.127	0.0041
UNIFAC	308.15	2.45	0.0167
Margules	323.15	0.077	0.0023
Van Laar	323.15	0.095	0.0027
Wilson	323.15	0.099	0.0028
NRTL	323.15	0.092	0.0026
UNIQUAC	323.15	0.097	0.0026
UNIFAC	323.15	2.06	0.0136

[a] δP, average absolute deviation of pressure; δy_1, average absolute deviation of vapor mole fraction.

deviations between the experimental results, the correlations of the five activity coefficient models, and interestingly the prediction using the UNIFAC model with parameters reported in the literature (*9*) are shown in Table V.

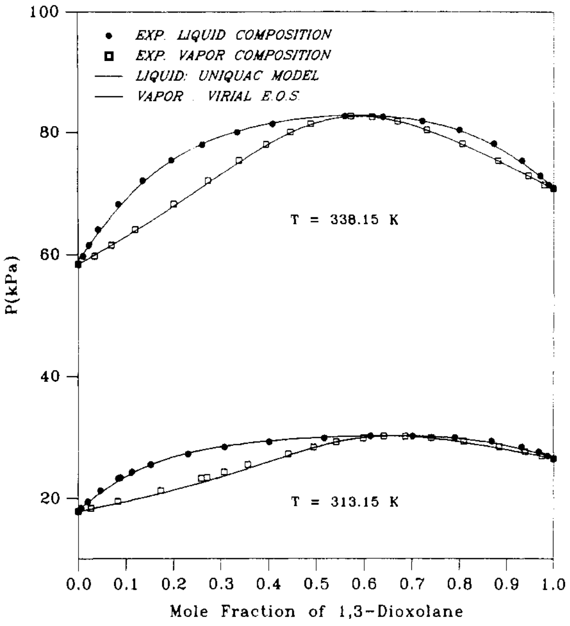

Figure 4. Vapor–liquid equilibrium of 1,3-dioxolane + ethanol at 313.15 and 338.15 K.

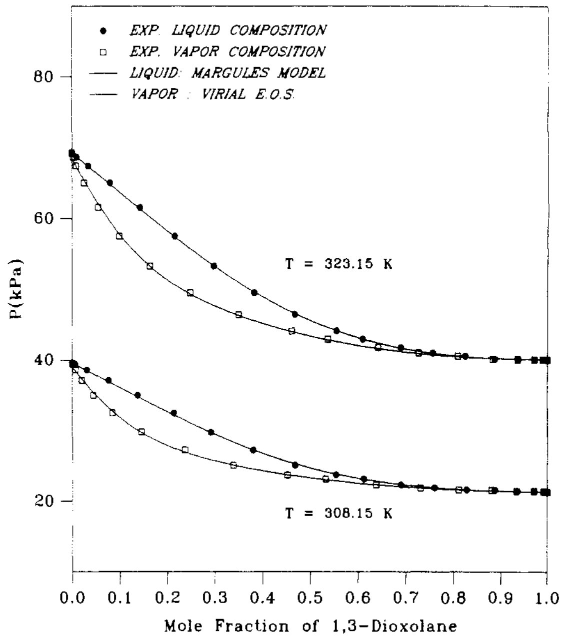

Figure 5. Vapor–liquid equilibrium of 1,3-dioxolane + chloroform at 308.15 and 323.15 K.

The Wilson model is generally the best for correlating mixtures of 1,3-dioxolane with hydrocarbons and with water. The UNIQUAC model gives the best correlation for 1,3-dioxolane and ethanol mixtures, while the Margules model best correlates the data for 1,3-dioxolane and chloroform mixtures. The predictive UNIFAC model with published interaction parameters gives poor predictions for all the mixtures studied here. This is undoubtedly the result of an interference between the two cyclic ether groups on the same molecule which violates the group contribution assumption.

Registry No. EtOH, 64-17-5; $CHCl_3$, 67-66-3; H_2O, 7732-18-5; 1,3-dioxolane, 646-06-0; cyclohexane, 110-82-7; heptane, 142-82-5.

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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*)	
$\ln P° = 13.1756 - 1357.14/(T - 134.33)$	
trichloroethylene (*4*)	
$\ln P° = 16.1827 - 3028.13/(T - 43.15)$	

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

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

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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