J. Chem. Eng. Data **2003,** *48,* 887−891

Vapor−Liquid Equilibrium and Volumetric Measurements for Binary Mixtures of 1,4-Dioxane with Isomeric Chlorobutanes

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Volumetric and isobaric vapor−liquid equilibrium measurements are reported for 1,4-dioxane + 1-chlorobutane, + 2-chlorobutane, + 2-methyl-1-chloropropane, and + 2-chloro-2-methylpropane. From density measurements, excess volumes have been calculated and correlated with a Redlich−Kister equation. The VLE data are thermodynamically consistent and were well correlated with Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations. The VLE results have been compared to the predictions by the UNIFAC and ASOG methods.

Introduction

We present here density and isobaric vapor−liquid equilibrium (VLE) measurements for the mixtures of 1,4-dioxane with isomeric chlorobutanes. The densities have been determined at the temperature of 298.15 K; the vapor−liquid equilibria have been studied at the pressures of 40.0 kPa (except for 2-chloro-2-methylpropane due to its low boiling temperature) and 101.3 kPa. In previous papers, we have reported isobaric VLE of binary mixtures containing 1,4-dioxane,[1] 1-chlorobutane,[2] or 2-chlorobutane.[3] We have found one reference for isothermal vapor−liquid equilibrium for 1-chlorobutane with 1,4-dioxane,[4] but no references at isobaric conditions. From density measurements, excess volumes have been calculated and correlated with a Redlich−Kister equation. The VLE experimental results have been checked for thermodynamic consistency, and the activity coefficients have been correlated with the following equations: Margules,[5] Van Laar,[6] Wilson,[7] NRTL,[8] and UNIQUAC.[9] The experimental results were used to test the prediction capability of the UNIFAC[10,11] and ASOG[12] group contribution methods.

Experimental Section

Materials. The liquids used were 1-chlorobutane (>99.5 mol %), 2-chlorobutane and 2-methyl-2-chloropropane (>99 mol %) obtained from Aldrich, and 1,4-dioxane (>99 mol %) and 2-methyl-1-chloropropane (>99 mol %) provided by Fluka. The purity of chemicals was checked by gas chromatography, and they were used without further purification.

Methods. Densities were measured with an Anton Paar DMA-58 vibrating tube densimeter automatically thermostated within ±0.01 K; the precision of density measurements is $\pm 5 \times 10^{-6}$ g·cm^{-3}, and the accuracy of these measurements after proper calibration is $\pm 10^{-5}$ g·cm^{-3}. The calibration was carried out with deionized twice-distilled water and dry air. The still used to study the vapor−liquid equilibrium was an all-glass dynamic recirculating type that was equipped with a Cottrell pump. It is a commercial unit (Labodest model) built in Germany

Table 1. Densities at 298.15 K, ρ, and Normal Boiling Points, T_b, of the Chemicals and Comparison with Literature Data

	ρ/g·cm^{-3}		T_b/K	
compound	expt	lit	expt	lit
1,4-dioxane	1.027 88	1.02797[a]	374.52	374.47[a]
1-chlorobutane	0.880 69	0.88095[a]	351.52	351.58[a]
2-chlorobutane	0.867 40	0.8671[b]	341.26	341.40[b]
2-methyl-1-chloropropane	0.871 13	0.8717[a]	342.05	342.0[a]
2-methyl-2-chloropropane	0.836 45	0.8361[a]	323.88	323.9[a]

[a] Reference 13. [b] Reference 14.

Table 2. Densities and Excess Volumes of 1,4-Dioxane (1) + Isomeric Chlorobutanes (2)

x_1	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}
1,4-Dioxane (1) + 1-Chlorobutane (2) at 298.15 K					
0.0422	0.885 61	0.022	0.6082	0.961 08	0.179
0.0947	0.891 80	0.053	0.6587	0.968 92	0.169
0.2055	0.905 35	0.109	0.7939	0.990 92	0.128
0.2766	0.914 45	0.134	0.8940	1.008 37	0.072
0.4083	0.932 02	0.174	0.9509	1.018 71	0.034
0.4852	0.942 87	0.181			
1,4-Dioxane (1) + 2-Chlorobutane (2) at 298.15 K					
0.0522	0.874 11	0.011	0.6155	0.957 41	0.026
0.0886	0.878 88	0.017	0.7149	0.974 47	0.016
0.1892	0.892 48	0.029	0.8019	0.990 07	0.006
0.2923	0.907 06	0.035	0.9068	1.009 72	-0.004
0.3647	0.917 71	0.036	0.9410	1.016 33	-0.006
0.4928	0.937 42	0.033			
1,4-Dioxane (1) + 2-Methyl-1-chloropropane (2) at 298.15 K					
0.0529	0.877 81	0.009	0.5945	0.955 19	0.086
0.1009	0.883 95	0.023	0.7005	0.972 78	0.075
0.2001	0.896 98	0.053	0.7926	0.988 80	0.062
0.3003	0.910 79	0.072	0.8978	1.008 04	0.040
0.3957	0.924 50	0.086	0.9371	1.015 61	0.020
0.5022	0.940 58	0.090			
1,4-Dioxane (1) + 2-Methyl-2-chloropropane (2) at 298.15 K					
0.0563	0.845 77	−0.112	0.6071	0.945 55	−0.486
0.1059	0.853 89	−0.171	0.7113	0.966 40	−0.417
0.2019	0.870 20	−0.290	0.8000	0.984 50	−0.307
0.3134	0.889 71	−0.377	0.9062	1.006 81	−0.131
0.4148	0.908 22	−0.433	0.9554	1.017 73	−0.062
0.5097	0.926 46	−0.489			

Table 3. Parameters, A_i, and Standard Deviations σ, for Equation 1

system	A_0	A_1	A_2	A_3	σ
1,4-dioxane + 1-chlorobutane	0.733	0.096	−0.062	−0.004	0.001
1,4-dioxane + 2-chlorobutane	0.135	-0.083	−0.076	−0.119	0.001
1,4-dioxane + 2-methyl-1-chloropropane	0.361	−0.011	−0.047	0.159	0.001
1,4-dioxane + 2-methyl-2-chloropropane	−1.927	−0.573	0.254	1.195	0.003

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10.1021/je020185k CCC: $25.00

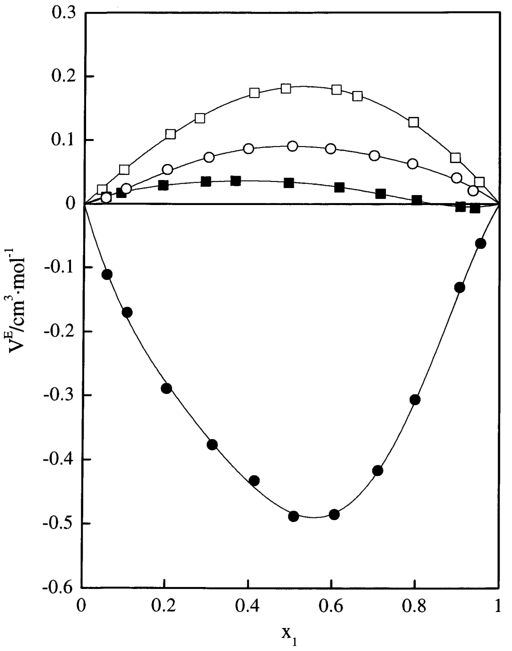

Figure 1. Excess volumes for 1,4-dioxane (1) + isomeric chlorobutanes (2) at T = 298.15 K as a function of mole fraction x_1: 1-chlorobutane (□); 2-chlorobutane (■); 2-methyl-1-chloropropane (○); 2-methyl-2-chloropropane (●).

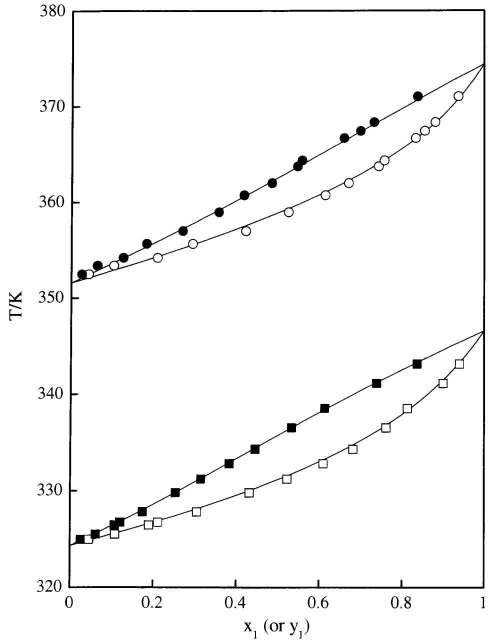

Figure 2. $T-x_1-y_1$ diagram for 1,4-dioxane (1) + 1-chlorobutane (2): (□, ■) experimental data at 40.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) Wilson equation.

by Fischer. The equilibrium temperatures were measured to an accuracy of ±0.01 K by means of a thermometer (model F25 with a PT100 probe) from Automatic Systems Laboratories, and the pressure in the still was measured with a pressure transducer Druck PDCR 110/W (pressure indicator DPI201) with an accuracy of ±0.1 kPa. The compositions of both phases, vapor and liquid, were determined by a densimetric analysis. The estimated uncertainty in the determination of both liquid- and vapor-phase mole fractions is ±0.0001.

The proper operation of the different devices was periodically checked and rearranged if necessary. The comparison of measured densities and normal boiling points of the chemicals with literature values[13,14] is shown in Table 1.

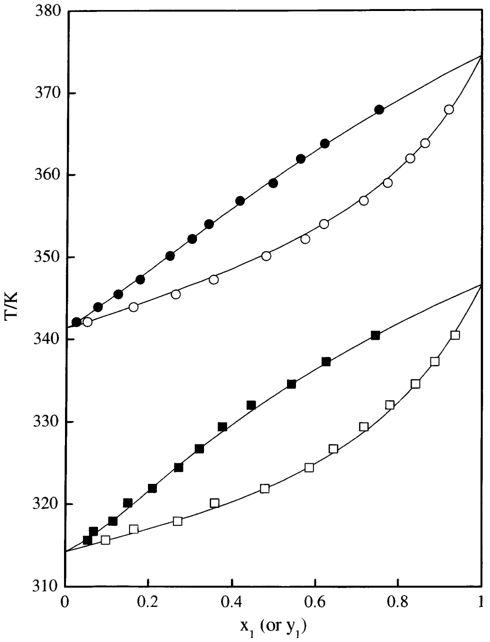

Figure 3. $T-x_1-y_1$ diagram for 1,4-dioxane (1) + 2-chlorobutane (2): (□, ■) experimental data at 40.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) Wilson equation.

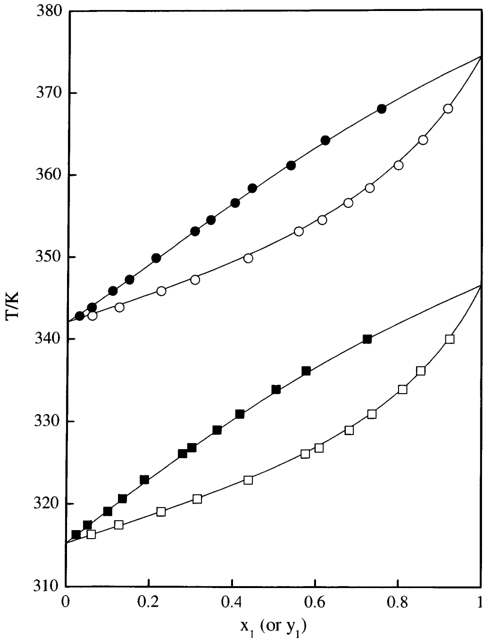

Figure 4. $T-x_1-y_1$ diagram for 1,4-dioxane (1) + 2-methyl-1-chloropropane (2): (□, ■) experimental data at 40.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) Wilson equation.

Results and Discussion

The experimental values of density together with the corresponding calculated excess volumes are given in Table 2, and excess volumes are graphically represented in Figure 1. For each mixture, the excess volumes were correlated by means of a Redlich−Kister equation,

$$V^{E}/\mathrm{cm}^{3}\cdot\mathrm{mol}^{-1} = x_1x_2\sum_{i=0}^{k}A_i(x_1 - x_2)^i \qquad (1)$$

Table 4. Isobaric VLE Data of 1,4-Dioxane (1) + Isomeric Chlorobutanes (2): Temperature T, Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, and Activity Coefficients γ_i

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
1,4-Dioxane (1) + 1-Chlorobutane (2) at 40.0 kPa														
324.94	0.0459	0.0259	1.307	0.997	329.80	0.4315	0.2539	1.117	1.075	338.56	0.8129	0.6135	1.016	1.253
325.49	0.1087	0.0620	1.291	1.007	331.24	0.5225	0.3149	1.079	1.117	341.15	0.9005	0.7393	1.003	1.459
326.44	0.1892	0.1078	1.240	1.017	332.84	0.6099	0.3833	1.056	1.164	343.19	0.9400	0.8368	1.008	1.418
326.73	0.2117	0.1210	1.229	1.020	334.32	0.6822	0.4456	1.036	1.221					
327.83	0.3047	0.1744	1.177	1.044	336.55	0.7616	0.5336	1.019	1.269					
1,4-Dioxane (1) + 1-Chlorobutane (2) at 101.3 kPa														
352.45	0.0424	0.0264	1.265	0.990	358.97	0.5256	0.3567	1.106	1.091	366.68	0.8339	0.6608	1.006	1.326
353.34	0.1031	0.0634	1.212	0.990	360.71	0.6150	0.4180	1.046	1.158	367.43	0.8558	0.7010	1.016	1.320
354.17	0.2075	0.1255	1.158	1.021	361.97	0.6712	0.4858	1.069	1.156	368.33	0.8815	0.7335	1.003	1.397
355.64	0.2931	0.1814	1.127	1.026	363.72	0.7441	0.5475	1.027	1.245	371.01	0.9378	0.8385	0.992	1.503
356.98	0.4225	0.2693	1.110	1.078	364.32	0.7577	0.5590	1.010	1.261					
1,4-Dioxane (1) + 2-Chlorobutane (2) at 40.0 kPa														
315.61	0.0980	0.0537	1.897	0.997	321.89	0.4779	0.2093	1.153	1.148	332.04	0.7792	0.4451	0.991	1.350
316.96	0.1650	0.0682	1.348	1.009	324.41	0.5845	0.2724	1.104	1.215	334.59	0.8404	0.5413	1.011	1.421
317.92	0.2703	0.1154	1.335	1.058	326.68	0.6429	0.3210	1.076	1.221	337.31	0.8871	0.6248	0.995	1.508
320.14	0.3581	0.1504	1.192	1.067	329.39	0.7167	0.3758	1.012	1.292	340.49	0.9360	0.7440	0.995	1.644
1,4-Dioxane (1) + 2-Chlorobutane (2) at 101.3 kPa														
342.05	0.0508	0.0247	1.433	1.002	350.10	0.4805	0.2498	1.146	1.112	358.93	0.7741	0.4970	1.047	1.342
343.80	0.1615	0.0762	1.304	1.020	352.15	0.5745	0.3021	1.079	1.191	361.90	0.8284	0.5634	1.006	1.417
345.38	0.2636	0.1251	1.238	1.049	353.96	0.6201	0.3425	1.065	1.195	363.74	0.8640	0.6216	1.003	1.476
347.17	0.3544	0.1778	1.227	1.067	356.78	0.7162	0.4174	1.022	1.311	367.88	0.9218	0.7533	0.999	1.505
1,4-Dioxane (1) + 2-Methyl-1-chloropropane (2) at 40.0 kPa														
316.33	0.0613	0.0246	1.346	1.000	322.93	0.4371	0.1884	1.086	1.091	330.92	0.7357	0.4167	1.028	1.268
317.50	0.1281	0.0523	1.300	1.002	326.12	0.5748	0.2795	1.072	1.147	333.92	0.8101	0.5038	1.002	1.360
319.09	0.2289	0.1011	1.312	1.013	326.83	0.6088	0.3019	1.062	1.178	336.17	0.8530	0.5756	0.996	1.397
320.61	0.3157	0.1361	1.199	1.038	328.99	0.6813	0.3619	1.042	1.228	340.03	0.9226	0.7249	1.001	1.522
1,4-Dioxane (1) + 2-Methyl-1-chloropropane (2) at 101.3 kPa														
342.77	0.0601	0.0293	1.399	1.012	349.81	0.4351	0.2124	1.087	1.108	358.34	0.7300	0.4445	1.013	1.287
343.83	0.1254	0.0592	1.303	1.020	353.07	0.5578	0.3068	1.094	1.135	361.10	0.8000	0.5392	1.024	1.337
345.82	0.2256	0.1091	1.242	1.028	354.45	0.6145	0.3453	1.066	1.182	364.16	0.8586	0.6223	0.997	1.430
347.17	0.3074	0.1491	1.186	1.055	356.55	0.6779	0.4033	1.051	1.217	367.96	0.9188	0.7594	1.008	1.438
1,4-Dioxane (1) + 2-Methyl-2-chloropropane (2) at 101.3 kPa														
325.60	0.0753	0.0251	1.870	0.997	337.55	0.5173	0.1706	1.151	1.134	351.27	0.8044	0.3971	1.045	1.399
328.79	0.2081	0.0590	1.396	1.017	339.49	0.5741	0.2029	1.146	1.169	357.85	0.8850	0.5245	1.002	1.589
330.36	0.2748	0.0796	1.339	1.036	341.32	0.6200	0.2290	1.118	1.204	359.80	0.8976	0.5710	1.008	1.535
331.47	0.3146	0.0916	1.287	1.046	343.99	0.6795	0.2691	1.087	1.257	365.28	0.9460	0.7083	0.994	1.736
334.33	0.4222	0.1277	1.195	1.094	346.85	0.7345	0.3135	1.056	1.319					

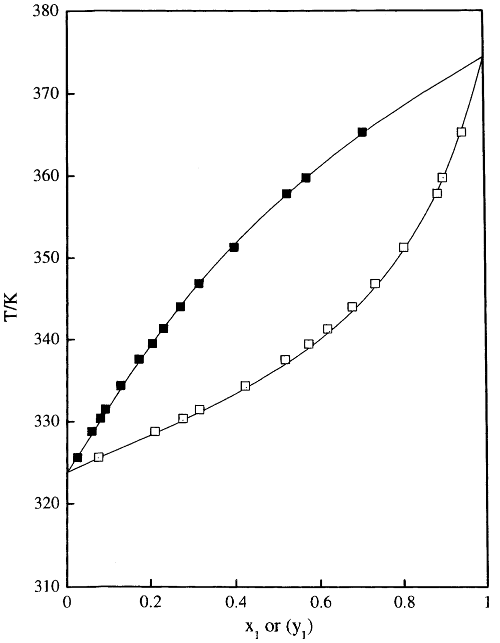

Figure 5. $T-x_1-y_1$ diagram for 1,4-dioxane (1) + 2-methyl-2-chloropropane (2): (□, ■) experimental data at 40.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) Wilson equation.

Values of the adjustable parameters A_i together with the standard deviations $\sigma(V^E)$ are presented in Table 3.

The excess volumes for the mixtures containing 1-chlorobutane and 2-methyl-1-chloropropane are positive over the whole composition range, for the mixture with 2-chlorobutane V^E is positive except at high mole fractions of 1,4-dioxane, and finally for the mixture containing 2-methyl-2-chloropropane excess volume is negative over the whole composition range.

Table 5. Constants of the Antoine Equation for Vapor Pressures of the Pure Compounds (Temperature in °C, Pressure in kPa)

compound	A	B	C
1,4-dioxane	6.5564	1554.679	240.337
1-chlorobutane	6.05154	1216.82	222.33
2-chlorobutane	6.1222	1245.2	234.4
2-methyl-1-chloropropane	6.01854	1176.06	224.125
2-methyl-2-chloropropane	5.99201	1114.899	229

The vapor−liquid equilibrium data, T, x_1, and y_1, along with activity coefficients, γ_i, are presented in Table 4, and the corresponding $T-x_1-y_1$ diagrams are shown in Figures 2−5.

The activity coefficients of the components in the liquid phase were calculated from the following equations:

$$\gamma_i = \frac{y_i P}{x_i p_i^o} \exp\left[\frac{(B_{ii} - V_i^o)(P - p_i^o) + (1 - y_i)^2 P \delta_{ij}}{RT}\right] \tag{2}$$

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{3}$$

x_i and y_i are the liquid- and vapor-phase compositions, P is the total pressure, p_i^o are the vapor pressures of the pure compounds calculated with the Antoine equation, where the constants are given in Table 5, B_{ii} are the second

Table 6. Results of the Thermodynamic Consistency Test: Average Deviations ΔP and Δy

system	P/kPa	ΔP/kPa	Δy
1,4-dioxane + 1-chlorobutane	40.0	0.4	0.0058
	101.3	0.8	0.0072
1,4-dioxane + 2-chlorobutane	40.0	0.7	0.0046
	101.3	0.9	0.0050
1,4-dioxane + 2-methyl-1-chloropropane	40.0	0.1	0.0055
	101.3	0.9	0.0047
1,4-dioxane + 2-methyl-2-chloropropane	101.3	1.4	0.0047

Table 7. Correlation Parameters: Average Deviations ΔT and Δy and Activity Coefficients at Infinite Dilution γ_i^∞

equation	A_{12}	A_{21}	ΔT/K	Δy	γ_1^∞	γ_2^∞
1,4-Dioxane (1) + 1-Chlorobutane (2) at 40.0 kPa						
Margules	0.3097^a	0.4179^a	0.24	0.0061	1.36	1.52
Van Laar	0.3171^a	0.4226^a	0.23	0.0061	1.37	1.53
Wilson	210.3719^b	1027.7572^b	0.24	0.0066	1.37	1.52
NRTL	2106.6635^b	−825.9000^b	0.24	0.0066	1.37	1.52
UNIQUAC	632.4198^b	−239.6217^b	0.24	0.0066	1.37	1.52
1,4-Dioxane (1) + 1-Chlorobutane (2) at 101.3 kPa						
Margules	0.2337^a	0.4537^a	0.22	0.0075	1.26	1.57
Van Laar	0.2602^a	0.4878^a	0.24	0.0078	1.30	1.63
Wilson	−437.9774^b	2169.7551^b	0.25	0.0083	1.29	1.63
NRTL	3558.2813^b	−1755.9739^b	0.24	0.0080	1.28	1.61
UNIQUAC	1556.4715^b	−930.1446^b	0.25	0.0082	1.29	1.64
1,4-Dioxane (1) + 2-Chlorobutane (2) at 40.0 kPa						
Margules	0.6053^a	0.4876^a	0.33	0.0050	1.83	1.63
Van Laar	0.6392^a	0.4792^a	0.33	0.0053	1.89	1.61
Wilson	2191.9805^b	−474.9112^b	0.32	0.0052	1.93	1.60
NRTL	−118.1348^b	1776.1762^b	0.32	0.0051	1.89	1.60
UNIQUAC	−725.6494^b	1478.6545^b	0.32	0.0052	1.91	1.61
1,4-Dioxane (1) + 2-Chlorobutane (2) at 101.3 kPa						
Margules	0.4086^a	0.5107^a	0.32	0.0058	1.50	1.67
Van Laar	0.4156^a	0.5126^a	0.32	0.0059	1.52	1.67
Wilson	563.9224^b	1015.8915^b	0.34	0.0070	1.52	1.66
NRTL	2159.7163^b	−555.9095^b	0.34	0.0068	1.51	1.66
UNIQUAC	544.1971^b	−46.6377^b	0.34	0.0070	1.51	1.66
1,4-Dioxane (1) + 2-Methyl-1-chloropropane (2) at 40.0 kPa						
Margules	0.3532^a	0.4827^a	0.12	0.0063	1.42	1.62
Van Laar	0.3641^a	0.4873^a	0.12	0.0064	1.44	1.63
Wilson	272.9585^b	1134.3635^b	0.15	0.0075	1.44	1.62
NRTL	2267.4732^b	−813.9134^b	0.14	0.0072	1.43	1.62
UNIQUAC	720.5493^b	−268.1797^b	0.15	0.0074	1.44	1.62
1,4-Dioxane (1) + 2-Methyl-1-chloropropane (2) at 101.3 kPa						
Margules	0.3817^a	0.4383^a	0.31	0.0061	1.46	1.55
Van Laar	0.3836^a	0.4397^a	0.31	0.0061	1.47	1.55
Wilson	672.7931^b	674.2691^b	0.35	0.0071	1.47	1.54
NRTL	1720.9601^b	−358.0122^b	0.34	0.0070	1.46	1.54
UNIQUAC	269.0213^b	159.4448^b	0.35	0.0071	1.47	1.54
1,4-Dioxane (1) + 2-Methyl-2-chloropropane (2) at 101.3 kPa						
Margules	0.5727^a	0.5719^a	0.42	0.0069	1.77	1.77
Van Laar	0.5728^a	0.5718^a	0.42	0.0069	1.77	1.77
Wilson	1320.4763^b	465.0420^b	0.38	0.0064	1.79	1.75
NRTL	1297.5334^b	435.3241^b	0.39	0.0066	1.78	1.73
UNIQUAC	−69.5714^b	647.3549^b	0.38	0.0065	1.78	1.75

^{a} Dimensionless. ^{b} $\mathrm{J \cdot mol^{-1}}$.

Table 8. VLE Predictions, Average Deviations ΔT and Δy

		UNIFAC		ASOG	
system	P/kPa	ΔT/K	Δy	ΔT/K	Δy
1,4-dioxane + 1-chlorobutane	40.0	3.40	0.0360	4.92	0.0515
	101.3	2.87	0.0370	4.86	0.0618
1,4-dioxane + 2-chlorobutane	40.0	2.67	0.0319	6.44	0.0757
	101.3	2.63	0.0314	6.40	0.0753
1,4-dioxane + 2-methyl-1-chloropropane	40.0	4.08	0.0420	5.64	0.0580
	101.3	3.37	0.0387	5.47	0.0657
1,4-dioxane + 2-methyl-2-chloropropane	101.3	1.30	0.0111	7.63	0.0702

virial coefficients, B_{ij} is the cross second virial coefficient calculated using a suitable mixing rule, and V_i^0 are the molar volumes of the saturated liquids. The contribution of the exponential term in eq 2 was important only at very dilute concentrations.

Antoine's constants for 1,4-dioxane, 2-methyl-1-chloropropane, and 2-methyl-2-chloropropane were obtained from Gmehling et al.[15,16] and for 1-chlorobutane and 2-chlorobutane were taken from Riddick et al.[14] The second virial coefficients were estimated by the Redlich−Kwong equation.[17] The molar volumes of the saturated liquids were calculated using the Yen and Woods method.[18]

The thermodynamic consistency of the experimental results was checked using the Van Ness method,[19] described by Fredenslund et al.[20] using a third-order Legendre polynomial for the excess Gibbs energies. According to this test, experimental data are considered consistent if the average deviation in y (Δy) is smaller than 0.01. All the experimental data are consistent, as one can see in Table 6.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations. Estimation of the parameters for all the equations was based on minimization of an objective function in terms of experimental and calculated γ_i values.[21] These adjustable parameters, A_{12} and A_{21} (see definitions in ref 15) along with the average deviation in T (ΔT), the average deviation in y (Δy), and the activity coefficients at infinite dilution, γ_i^∞, are listed in Table 7. Since the average deviation in temperature is less than 0.5 K and that of the vapor composition is less than 0.01, all the equations correlated the activity coefficients quite well.

The systems present positive deviations from ideality. In the temperature diagrams, it can be seen that the systems do not show azeotropes.

VLE Predictions

The UNIFAC and ASOG methods were used to predict the vapor−liquid equilibrium of the systems studied. The temperature and vapor-phase composition obtained experimentally were compared with the theoretical predictions using the UNIFAC and ASOG methods; in Table 8 the average deviations in temperature and vapor-phase composition are given. Neither UNIFAC nor ASOG gives satisfactory predictions, although they are better for UNIFAC than for ASOG. It is necessary, therefore, to keep enlarging the database used to calculate the parameters of the two methods to attain a better description of the VLE behavior of these kinds of liquid mixtures.

Literature Cited

(1) Gascón, I.; Domínguez, M.; Cea, P.; López, M. C.; Royo, F. M. Isobaric (vapour + liquid) equilibrium of (1,3-dioxolane, or 1,4-dioxane + 1-butanol, or 2-butanol) at 40.0 kPa and 101.3 kPa. *J. Chem. Thermodyn.* **2001**, *33*, 1361−1373.

(2) Artigas, H.; Lafuente, C.; López, M. C.; Royo, F. M.; Urieta, J. S. Isobaric vapor−liquid equilibria for binary mixtures of 1-chlorobutane with isomeric butanols at 40.0 and 101.3 kPa. *J. Chem. Eng. Data* **1994**, *39*, 729−732.

(3) Cea, P.; Lafuente, C.; Sanz, M. L.; Royo, F. M.; Urieta, J. S. Isobaric vapor−liquid equilibrium measurements on 2-chlorobutane + isomeric butanols at 60.0 and 101.3 kPa. *J. Chem. Eng. Data* **1995**, *40*, 692−695.

(4) Gutsche, B.; Knapp, H. Measurement of vapor−liquid equilibria: Chlorohydrocarbons and aliphatic ethers. *EFCE Publ. Ser.* **1980**, *11*, 62−67.

(5) Margules, M. *S.-B. Akad. Wiss. Wien, Math.-Naturwiss. KI. II.* **1895**, *104*, 1234.

(6) Van Laar, J. J. Vapour pressure of binary mixtures. *Z. Phys. Chem.* **1910**, *72*, 723−751.

(7) Wilson, G. M. A new expression for the excess Gibbs free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

(8) Renon, H.; Prausnitz, J. M. Local composition in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.

(9) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures. New expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116−128.

(10) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J.* **1975**, *21*, 1086−1099.
(11) Gmehling, J.; Li, J.; Schiller, M. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.
(12) Tochigi, K.; Tiegs, D.; Gmehling, J.; Kojima, K. Determination of new ASOG parameters. *J. Chem. Eng. Jpn.* **1990**, *23*, 453−463.
(13) *TRC Thermodynamic Tables*: *Non-Hydrocarbons*, *Selected Values of Properties of Chemical Compounds*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1983; p a-7040.
(14) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Techniques of Chemistry, Vol. II; Wiley-Interscience: New York, 1986; pp 312, 471−475.
(15) Gmehling, J.; Onken, U.; Arlt, W. *Vapor−liquid equilibrium data collection*; DECHEMA Chemistry Data Series, Vol. I, Part 1a; DECHEMA: Frankfurt/Main, 1981; pp xxvi−xxx, 556.
(16) Gmehling, J.; Onken, U.; Arlt, W. *Vapor−liquid equilibrium data collection*; DECHEMA Chemistry Data Series, Vol. I, Part 8; DECHEMA: Frankfurt/Main, 1981; pp 125, 321.
(17) Redlich, O.; Kwong, J. N. S. The thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. *Chem. Rev.* **1949**, *44*, 233−244.
(18) Yen, L. C.; Woods, S. S. A generalized equation for computer calculation of liquid densities. *AIChE J.* **1968**, *12*, 95−99.
(19) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor−liquid equilibria. I. Appraisal of data reduction methods. *AIChE J.* **1973**, *19*, 238−244.
(20) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977; pp 68−74.
(21) Silverman, N.; Tassios, D. P. Prediction of multicomponent VLE with the Wilson equation. Effect of the minimization function and of the quality of binary data. *Ind. Eng. Chem. Process Des. Dev.* **1984**, *23*, 586−589.

Received for review September 24, 2002. Accepted April 10, 2003. This work was financially supported by IBERCAJA (IBE2002-CIEN-02), for which the authors are very grateful.

JE020185K