Table IV. Coordinates of Three-Phase Equilibrium and of Homogeneous Azeotropy for Water (1)/Methyl Acetate (2) at 50 °C

P^*, kPa (measured)	78.30
x_1^{α} (calculated)	0.3400
x_1^{β} (calculated)	0.9313
y_1^* (calculated)	0.1542
P^{az}, kPa (calculated)	80.604
x_1^{az} (calculated)	0.0876

All curves were generated from the equilibrium equations, with parameters for eq 2 as given in Table III. Values of significant pressure and composition coordinates are summarized in Table IV.

Glossary

A_{12}, A_{21}	parameters in eq 2
$\hat{a}_i^{\alpha}$, $\hat{a}_i^{\beta}$	liquid-phase activities at miscibility limits
B_{11}, B_{22}, B_{12}	second virial coefficients
G^E	excess Gibbs function, liquid phase
g	G^E/RT
P	total pressure
P^{az}	azeotropic pressure
P^*	three-phase equilibrium pressure
P_i^{sat}	vapor pressure of pure i
R	universal gas constant
T	absolute temperature
V_i^L	molar volume of pure liquid i
x_i	mole fraction, liquid phase
x_i^{az}	azeotropic composition
x_i^{α}, x_i^{β}	liquid miscibility limits
y_i^*	vapor-phase mole fraction at three-phase equilibrium

Greek Letters

α_{12}, α_{21}	parameters in eq 2
γ_i	activity coefficient, liquid phase
γ_i^{α}, γ_i^{β}	liquid-phase activity coefficients at miscibility limits
δ	denotes the difference, calculated - experimental
Φ_i	correction factors in the equation for VLE
Φ_i^*	Φ_i, evaluated at conditions of three-phase equilibrium

Registry No. Methyl acetate, 79-20-9.

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Excess Thermodynamic Functions for Ternary Systems. 8. Total-Pressure Data and G^E for Ethanol/Chloroform/1,4-Dioxane at 50 °C

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Isothermal P-x data for the ternary system ethanol/chloroform/1,4-dioxane at 50 °C are reported, together with data for the constituent binaries. Data reduction by Barker's method provides a correlation for G^E.

Reported here are vapor/liquid equilibrium (VLE) measurements for the ethanol (1)/chloroform (2)/1,4-dioxane (3) system at 50 °C. Experimental values of total vapor pressure are presented for the full composition range of the three constituent binaries and for five runs with ternary mixtures formed by addition of a pure species to mixtures of the other two. The apparatus is that of Gibbs and Van Ness (*1*) as modified by DiElsi et al. (*2*).

Reagent-quality ethanol was supplied by U.S. Industrial Chemicals and chromatoquality chloroform and dioxane came from Matheson Coleman and Bell. Except for thorough degassing, all were used as received with minimum indicated purity of 99.9 mol %.

Table I. P-x Data for Ethanol (1)/Chloroform (2) at 50 °C

x_1	x_2	P, kPa	x_1	x_2	P, kPa
0.0208	0.9792	70.783	0.5505	0.4495	65.106
0.1017	0.8983	72.808	0.6004	0.3996	62.858
0.1523	0.8477	72.883	0.6508	0.3492	60.115
0.2029	0.7971	72.639	0.7010	0.2990	56.862
0.2532	0.7468	72.152	0.7512	0.2488	52.985
0.3036	0.6964	71.485	0.7984	0.2016	48.888
0.3536	0.6464	70.653	0.8517	0.1483	43.829
0.4032	0.5968	69.627	0.9014	0.0986	38.849
0.4532	0.5468	68.367	0.9481	0.0519	34.254
0.4998	0.5002	66.978	0.9805	0.0195	31.237
0.5026	0.4974	66.856			

Results and Correlations

Tables I-III give experimental values of total pressure for the three constituent binary systems, and Table IV shows the data for ternary mixtures. Data reduction is by Barker's method, as described earlier (*3*, *4*). For the binary systems, the

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Table II. P-x Data for Ethanol (1)/1,4-Dioxane (3) at 50 °C

x_1	x_3	P, kPa	x_1	x_3	P, kPa
0.0218	0.9782	16.826	0.5003	0.4997	28.664
0.0517	0.9483	18.244	0.5972	0.4028	29.550
0.1023	0.8977	20.305	0.6472	0.3528	29.892
0.1522	0.8478	22.019	0.6969	0.3031	30.162
0.2022	0.7978	23.476	0.7466	0.2534	30.371
0.2655	0.7345	25.025	0.7968	0.2032	30.505
0.3016	0.6984	25.764	0.8449	0.1551	30.535
0.3532	0.6468	26.698	0.8999	0.1001	30.425
0.4024	0.5976	27.452	0.9496	0.0504	30.108
0.4518	0.5482	28.103	0.9794	0.0206	29.804
0.4986	0.5014	28.677			

Table III. P-x Data for Chloroform (2)/1,4-Dioxane (3) at 50 °C

x_2	x_3	P, kPa	x_2	x_3	P, kPa
0.0282	0.9718	16.183	0.5491	0.4509	34.244
0.0614	0.9386	16.770	0.5988	0.4012	37.525
0.1006	0.8994	17.514	0.6488	0.3512	41.170
0.1507	0.8493	18.575	0.6987	0.3013	45.092
0.2506	0.7494	21.117	0.7491	0.2509	49.262
0.3001	0.6999	22.622	0.7985	0.2015	53.486
0.3558	0.6442	24.603	0.8480	0.1520	57.676
0.3994	0.6006	26.365	0.8959	0.1041	61.637
0.4497	0.5503	28.686	0.9474	0.0526	65.646
0.5001	0.4999	31.325	0.9789	0.0211	67.910

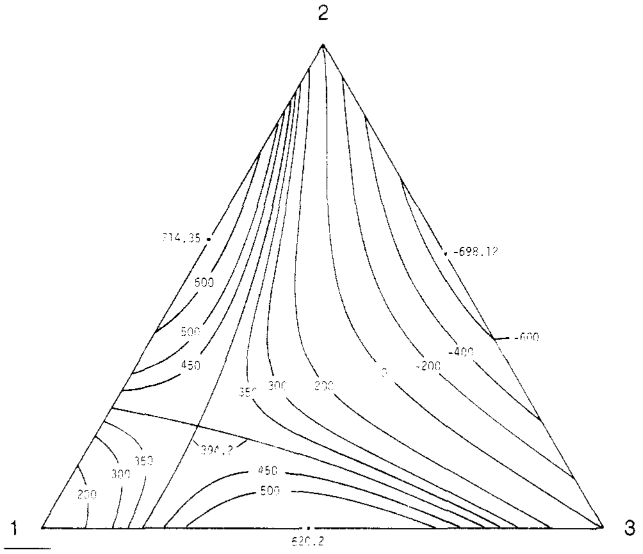

Figure 1. Lines of constant G^E (J/mol) for the ethanol (1)/chloroform (2)/1,4-dioxane (3) system at 50 °C.

Table IV. P-x Data for Ethanol (1)/Chloroform (2)/1,4-Dioxane (3) at 50 °C

x_1	x_2	x_3	P, kPa
0.2962	0.0206	0.6832	26.117
0.2873	0.0500	0.6627	26.608
0.2720	0.1004	0.6276	27.602
0.2570	0.1502	0.5928	28.734
0.2420	0.1998	0.5582	30.040
0.2269	0.2497	0.5234	31.528
0.2119	0.2993	0.4888	33.223
0.1967	0.3495	0.4538	35.179
0.1816	0.3993	0.4190	37.124
0.1666	0.4490	0.3844	39.799
0.1515	0.4990	0.3495	42.488
0.6840	0.0232	0.2928	30.958
0.6582	0.0600	0.2818	32.235
0.6259	0.1061	0.2680	33.999
0.5910	0.1559	0.2531	36.180
0.5417	0.2263	0.2320	39.624
0.5169	0.2617	0.2214	41.496
0.4849	0.3074	0.2077	44.043
0.4525	0.3536	0.1938	46.732
0.4181	0.4028	0.1791	49.653
0.3831	0.4528	0.1641	52.602
0.3484	0.5024	0.1492	55.433
0.0209	0.2927	0.6865	23.866
0.0509	0.2837	0.6654	25.324
0.1008	0.2688	0.6304	27.367
0.1507	0.2539	0.5954	28.993
0.2003	0.2390	0.5607	30.275
0.2494	0.2244	0.5263	31.302
0.2998	0.2092	0.4909	32.131
0.3502	0.1942	0.4556	32.783
0.3995	0.1795	0.4210	33.299
0.4499	0.1644	0.3857	33.697
0.4998	0.1495	0.3507	33.982
0.0202	0.6856	0.2942	46.673
0.0500	0.6648	0.2852	48.013
0.1004	0.6295	0.2701	49.597
0.1487	0.5957	0.2556	50.519
0.1989	0.5606	0.2405	51.043
0.2491	0.5255	0.2254	51.229
0.2995	0.4902	0.2103	51.175
0.3493	0.4554	0.1953	50.923
0.3991	0.4205	0.1804	50.502
0.4492	0.3855	0.1653	49.904
0.4992	0.3505	0.1503	49.155
0.2941	0.6862	0.0197	70.062
0.2846	0.6642	0.0512	67.429
0.2695	0.6292	0.1013	62.867
0.2544	0.5939	0.1517	58.205
0.2395	0.5595	0.2010	53.721
0.2227	0.5203	0.2570	48.920
0.2097	0.4901	0.3002	45.551
0.1946	0.4547	0.3507	41.898
0.1797	0.4199	0.4004	38.674
0.1646	0.3847	0.4507	35.763
0.1496	0.3497	0.5007	33.179

Margules equation with up to five parameters provides suitable expression of G^E:

$$g_{ij} \equiv G^E_{ij}/RT = [A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_ix_j + \eta(x_ix_j)^2]x_ix_j \qquad (1)$$

For the ethanol (1)/chloroform (2) system, correlation requires the full five parameters; for chloroform (2)/1,4-dioxane (3), $\eta = 0$; and for ethanol (1)/1,4-dioxane (3), $\eta = 0$ and $\lambda_{13} = \lambda_{31}$.

Data for the ternary system are adequately correlated by the three-parameter Wohl equation:

$$g_{123} = g_{12} + g_{13} + g_{23} + (C_0 + C_1x_1 + C_2x_2)x_1x_2x_3 \qquad (2)$$

Correlations for the g_{ij} are given by eq 1; parameters C_0, C_1, and C_2 result from regression of just the ternary data.

Second virial coefficients B_{ij} required for estimation of vapor-phase nonidealities come from the correlation of Hayden and O'Connell (*5*).

Results of correlation for the binary systems, together with all ancillary information, are summarized in Table V. With parameters for the binary systems fixed at the values of Table V, the ternary-mixture data are correlated when the parameters of eq 2 have the following values: $C_0 = 0.8268$; $C_1 = -1.2783$; $C_2 = -1.9109$. The root-mean-square (rms) value of δP for the ternary data is 0.112 kPa; the maximum value of $|\delta P|$ is 0.353 kPa.

Discussion

The only data extant directly comparable with ours are those reported by Van Ness and Abbott (*6*) for ethanol/chloroform and for ethanol/1,4-dioxane. In each case the present and earlier correlations yield pressures in excellent agreement, the maximum discrepency for each system being 0.16 kPa. The present data sets are correlated with considerably greater precision.

The results of this study are shown in Figures 1–3. Figure 1 is a contour diagram showing lines of constant G^E on a tri-

Table V. Summary of Results for Binary Systems at 50 °C[a]

	ethanol (1)/ chloroform (2)	ethanol (1)/1,4-dioxane (3)	chloroform (2)/1,4-dioxane (3)
P_i^{sat}, kPa	29.510	29.510	69.356
P_j^{sat}, kPa	69.356	15.697	15.697
V_i^L, cm³/mol	60	60	83
V_j^L, cm³/mol	83	88	88
B_{ii}, cm³/mol	-1400	-1400	-957
B_{jj}, cm³/mol	-957	-1385	-1385
B_{ij}, cm³/mol	-669	-929	-1600
A_{ij}	1.64064	0.86523	-0.76554
A_{ji}	0.52259	1.05535	-1.22615
λ_{ij}	0.94110	0.15773	-0.08087
λ_{ji}	-0.02453	0.15773	0.28857
η	0.82660		
rms δP, kPa	0.009	0.008	0.007
max $\lvert\delta P\rvert$, kPa	0.017	0.026	0.017

[a] Pairs of components are listed in the order i,j.

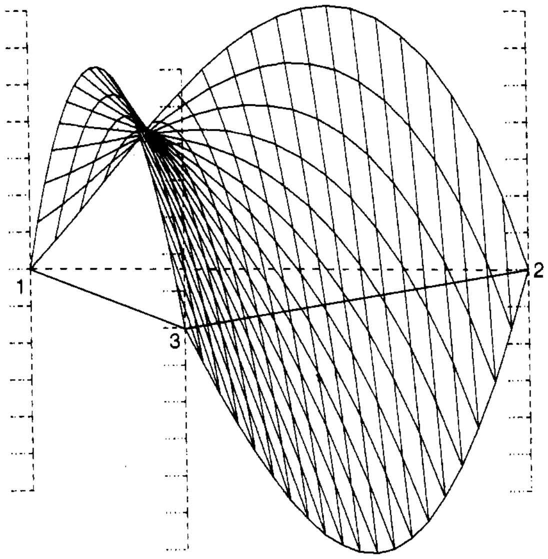

Figure 2. Pictorial view of the G^E–x surface for the ethanol (1)/chloroform (2)/1,4-dioxane (3) system at 50 °C.

angular mole fraction grid. Figure 2 is an oblique view of the same surface, and Figure 3 is a contour diagram showing lines of constant P.

The ethanol (1)/chloroform (2) system exhibits an azeotrope at x_1 = 0.1359, p^{az} = 72.912 kPa, as does the ethanol (1)/1,4-dioxane (3) system at x_1 = 0.8350, P_{az} = 30.539 kPa. Neither the chloroform (2)/1,4-dioxane (3) nor the ternary system has an azeotrope.

Glossary

A_{ij}, A_{ji}	parameters in eq 1
B_{ij}	second virial coefficient
C_0, C_1, C_2	parameters in eq 2
G^E	excess Gibbs function, liquid phase
g	G^E/RT
P	total pressure
P_i^{sat}	vapor pressure of pure i
R	universal gas constant
T	absolute temperature
V_i^L	molar volume of pure liquid i
x	mole fraction, liquid phase

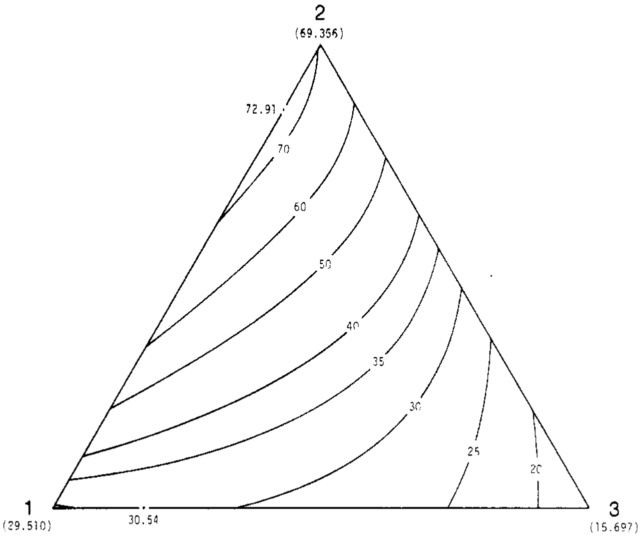

Figure 3. Lines of constant P (kPa) for the ethanol (1)/chloroform (2)/1,4-dioxane (3) system at 50 °C.

Greek Letters

λ_{ij}, λ_{ji}, η	parameters in eq 1
δ	denotes the difference, calculated – experimental

Registry No. Ethanol, 64-17-5; chloroform, 67-66-3; 1,4-dioxane, 123-91-1.

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