for the various calculations are given by Münster (*12*).

Glossary

Λ_{ij}	constant in Wilson equation
A_{ij}	binary constant in Margules equation
C	ternary constant in Margules equation
P	total pressure
P°	vapor pressure
x	mole fraction, liquid
y	mole fraction, vapor
γ	activity coefficient

Registry No. $(CH_3O)_3B$, 121-43-7; CH_3OH, 67-56-1; C_6H_6, 71-43-2.

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Excess Thermodynamic Functions for Ternary Systems. 10. H^E and S^E for Ethanol/Chloroform/1,4-Dioxane at 50 °C

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Heat-of-mixing data for the ternary liquid system ethanol/chloroform/1,4-dioxane at 50 °C are reported, along with data for the constituent binaries. A correlation of these data, together with a similar correlation for G^E, allows calculation of S^E values.

We report heat-of-mixing data at 50 °C for the ethanol (1)/chloroform (2)/1,4-dioxane (3) system. Experimental values are presented for the full composition range of each constituent binary liquid system and for nine runs with ternary liquid mixtures formed by addition of a pure species to a mixture of the other two. The apparatus is essentially that of Winterhalter and Van Ness (*1*).

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

Results and Correlations

Tables I–III give experimental values of H^E for the three constituent binary systems, and Table IV shows the data for ternary mixtures. These data, like the data for G^E reported earlier (*2*), are well correlated by equations of the form

$$M^E_{ij}/RT = [A_{ji}x_i + A_{ij}x_j - (D_{ji}x_i + D_{ij}x_j)x_ix_j + (E_{ji}x_i + E_{ij}x_j)(x_ix_j)^2]x_ix_j \quad (1)$$

$$M^E_{123}/RT = M^E_{12}/RT + M^E_{13}/RT + M^E_{23}/RT + x_1x_2x_3C \quad (2)$$

where

$$C = C_0 + C_1x_1 + C_2x_2 + C_3x_1^2 + C_4x_2^2 + C_5x_1x_2 \quad (3)$$

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

x_1	x_2	H^E, J mol^{-1}	x_1	x_2	H^E, J mol^{-1}
0.0288	0.9712	254.1	0.5985	0.4015	−3.7
0.0560	0.9440	430.4	0.6165	0.3836	−46.2
0.1125	0.8875	645.7	0.6316	0.3685	−85.1
0.1587	0.8413	719.9	0.6644	0.3356	−159.0
0.2191	0.7809	734.1	0.7156	0.2845	−262.2
0.2457	0.7543	719.7	0.7625	0.2375	−330.9
0.3144	0.6856	641.7	0.8173	0.1827	−369.4
0.3586	0.6414	567.2	0.8558	0.1442	−361.9
0.4017	0.5983	481.1	0.9006	0.0994	−309.7
0.4437	0.5563	386.6	0.9238	0.0762	−262.4
0.4960	0.5040	259.0	0.9483	0.0517	−196.1
0.5216	0.4784	195.7	0.9681	0.0319	−130.3
0.5481	0.4520	126.0	0.9893	0.0107	−47.8
0.5690	0.4310	73.8			

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

x_1	x_3	H^E, J mol^{-1}	x_1	x_3	H^E, J mol^{-1}
0.0093	0.9907	0 63.2	0.5383	0.4617	1602.0
0.0292	0.9708	1192.2	0.5651	0.4349	1586.4
0.0520	0.9480	333.1	0.5878	0.4122	1564.6
0.0758	0.9242	469.8	0.6215	0.3785	1524.2
0.1006	0.8994	607.9	0.6243	0.3757	1518.2
0.1397	0.8603	799.3	0.6743	0.3257	1430.1
0.1845	0.8155	995.4	0.7758	0.2242	1152.0
0.2316	0.7684	1168.1	0.8211	0.1789	983.4
0.2856	0.7144	1331.0	0.8631	0.1369	799.4
0.3364	0.6636	1450.1	0.9094	0.0906	566.1
0.3890	0.6110	1536.9	0.9481	0.0519	343.2
0.4380	0.5620	1587.6	0.9721	0.0279	191.2
0.4859	0.5141	1608.9	0.9893	0.0107	75.6

Heat-of-mixing data for the three binary systems are well correlated by eq 1 ($M^E_{ij} \equiv H^E_{ij}$) with the parameters listed in Table V. Combination of these parameters with the corresponding parameters for G^E_{ij} (*2*) in accord with the equation

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

x_2	x_3	H^E, J mol^{-1}	x_2	x_3	H^E, J mol^{-1}
0.0030	0.9970	−13.2	0.5273	0.4727	−1938.3
0.0151	0.9849	−75.0	0.5555	0.4445	−1955.2
0.0351	0.9649	−163.2	0.5735	0.4265	−1972.4
0.0645	0.9355	−303.5	0.6179	0.3821	−1966.9
0.0923	0.9077	−440.5	0.6744	0.3256	−1897.4
0.1226	0.8774	−584.5	0.7265	0.2735	−1768.5
0.1649	0.8351	−780.2	0.7773	0.2227	−1575.8
0.2150	0.7850	−1008.6	0.8255	0.1745	−1338.4
0.2652	0.7348	−1218.3	0.8728	0.1272	−1047.4
0.3111	0.6889	−1393.7	0.9060	0.0940	−809.6
0.3629	0.6371	−1564.3	0.9324	0.0676	−601.9
0.4146	0.5854	−1716.4	0.9519	0.0481	−439.4
0.4659	0.5341	−1835.5	0.9698	0.0302	−282.5
0.5149	0.4851	−1917.7	0.9890	0.0110	−105.9

$TS^E = H^E - G^E$ yields parameters in eq 1 for $M^E_{ij} \equiv TS^E_{ij}$; these are also listed in Table V.

Similarly, regression of just the ternary heat-of-mixing data by eq 2 ($M^E_{123} \equiv H^E_{123}$) yields the parameters C_0 through C_5 in eq 3 given in Table VI. Also given are the parameters C_0 through C_5 for $M^E_{123} \equiv TS^E_{123}$ determined from the correlations for H^E_{123} and G^E_{123}.

Discussion

Literature data directly comparable with ours exist for all three binary systems at 50 °C. The data of Shatas et al. (*3*) for ethanol/chloroform are generally in good agreement with ours; the two correlations differ by a maximum of about 28 J mol^{-1}. The H^E values of Belousov and Makarova (*4*) for ethanol/1,4-dioxane are lower than ours with a maximum difference of about 100 J mol^{-1}. McGlashan and Rastogi (*5*) report 6 H^E values for 1,4-dioxane/chloroform; except for one anomalous value, they differ by less than 90 J mol^{-1} from values given by our correlation.

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

x_1	x_2	x_3	H^E, J mol^{-1}	x_1	x_2	x_3	H^E, J mol^{-1}
0.0072	0.4489	0.5439	−1753.7	0.2644	0.1796	0.5560	284.4
0.0284	0.4394	0.5322	−1592.6	0.2782	0.1367	0.5851	534.2
0.0491	0.4300	0.5209	−1445.6	0.2930	0.0909	0.6161	818.8
0.0775	0.4172	0.5053	−1257.2	0.2997	0.0702	0.6301	950.8
0.1083	0.4033	0.4884	−1067.7	0.3057	0.0515	0.6428	1071.2
0.1492	0.3847	0.4661	−842.5	0.3197	0.0081	0.6722	1363.0
0.1963	0.3635	0.4402	−617.0	0.2813	0.4633	0.2554	−543.6
0.2455	0.3412	0.4133	−413.4	0.2961	0.4352	0.2687	−494.8
0.2945	0.3191	0.3864	−240.8	0.3225	0.3848	0.2927	−377.1
0.3408	0.2981	0.3611	−102.3	0.3497	0.3328	0.3175	−215.6
0.3891	0.2762	0.3347	19.0	0.3749	0.2849	0.3402	−32.3
0.4412	0.2527	0.3061	125.3	0.3982	0.2403	0.3615	165.6
0.4940	0.2288	0.2772	208.8	0.4190	0.2006	0.3804	362.7
0.5508	0.2032	0.2460	273.8	0.4425	0.1558	0.4017	607.0
0.0128	0.7508	0.2364	−1548.2	0.4632	0.1163	0.4205	839.6
0.0457	0.7258	0.2285	−1316.9	0.4820	0.0805	0.4375	1063.9
0.0850	0.6959	0.2191	−1083.0	0.4925	0.0605	0.4470	1194.5
0.1132	0.6745	0.2123	−941.9	0.5041	0.0383	0.4576	1342.2
0.1641	0.6358	0.2001	−730.0	0.5196	0.0087	0.4717	1546.2
0.2109	0.6002	0.1889	−580.5	0.1646	0.3982	0.4372	−823.0
0.2612	0.5619	0.1769	−455.4	0.1800	0.4356	0.3844	−839.6
0.3177	0.5190	0.1633	−348.0	0.1952	0.4722	0.3326	−825.1
0.3822	0.4699	0.1479	−260.9	0.2098	0.5077	0.2825	−773.2
0.4505	0.4179	0.1316	−200.7	0.2244	0.5429	0.2327	−677.3
0.0140	0.2334	0.7526	−997.3	0.2383	0.5765	0.1852	−533.6
0.0530	0.2242	0.7228	−727.9	0.2516	0.6086	0.1398	−340.8
0.0779	0.2183	0.7038	−569.4	0.2652	0.6415	0.0933	−80.2
0.1073	0.2113	0.6814	−395.3	0.2728	0.6600	0.0672	97.8
0.1541	0.2002	0.6457	−145.6	0.2800	0.6774	0.0426	290.0
0.2373	0.1805	0.5822	220.2	0.2896	0.7005	0.0099	574.3
0.2935	0.1672	0.5393	415.5	0.2685	0.2521	0.4794	−31.9
0.3539	0.1529	0.4932	582.9	0.2906	0.2728	0.4366	−76.7
0.4000	0.1420	0.4580	682.2	0.3156	0.2963	0.3881	−128.9
0.4498	0.1302	0.4200	763.3	0.3412	0.3203	0.3385	−179.0
0.5047	0.1172	0.3781	823.3	0.3661	0.3438	0.2901	−220.0
0.5553	0.1053	0.3394	852.1	0.3906	0.3667	0.2427	−246.4
0.6083	0.0927	0.2990	854.6	0.4284	0.4023	0.1693	−240.9
0.4437	0.3983	0.1580	−234.7	0.4505	0.4230	0.1265	−198.4
0.4768	0.3534	0.1698	−187.2	0.4718	0.4430	0.0852	−119.3
0.5163	0.2998	0.1839	−90.5	0.4874	0.4577	0.0549	−30.0
0.5532	0.2498	0.1970	40.6	0.5000	0.4694	0.0306	62.7
0.5899	0.2001	0.2100	210.4	0.5118	0.4805	0.0077	169.0
0.6282	0.1481	0.2237	430.7	0.4031	0.1340	0.4629	732.6
0.6633	0.1005	0.2362	668.6	0.4238	0.1409	0.4353	701.0
0.6825	0.0744	0.2431	811.5	0.4580	0.1522	0.3898	633.8
0.7021	0.0478	0.2501	968.2	0.4989	0.1658	0.3353	533.6
0.7294	0.0108	0.2598	1201.4	0.5390	0.1792	0.2818	415.8
0.1553	0.5181	0.3266	−1006.5	0.5777	0.1920	0.2303	285.9
0.1699	0.4728	0.3573	−925.2	0.6129	0.2037	0.1834	156.9
0.1865	0.4215	0.3920	−793.3	0.6447	0.2143	0.1410	36.2
0.2042	0.3666	0.4292	−610.2	0.6781	0.2254	0.0965	−90.4
0.2210	0.3144	0.4646	−398.8	0.6962	0.2314	0.0724	−155.5
0.2366	0.2660	0.4974	−175.0	0.7141	0.2374	0.0486	−215.8
0.2502	0.2237	0.5261	41.1	0.7390	0.2456	0.0154	−288.8

Table V. Correlating Parameters in Eq 1 for Binary Systems at 50 °C[a]

	ethanol (1)/ chloroform (2)	ethanol (1)/ 1,4-dioxane (3)	chloroform (2)/ 1,4-dioxane (3)
	$M^E_{ij} \equiv H^E_{ij}$		
A_{ij}	3.8040	2.5370	−1.6566
A_{ji}	−1.7287	2.6452	−3.5918
D_{ij}	10.3401	0.5564	2.0607
D_{ji}	1.0374	0.9879	1.5017
E_{ij}	16.5195	0.0	7.9875
E_{ji}	7.7294	0.0	−0.2473
σ, J mol^{-1}	1.05	0.64	2.47
max dev, J mol^{-1}	1.80	1.77	6.28
	$M^E_{ij} \equiv TS^E_{ij}$		
A_{ij}	2.1633	1.6718	−0.8911
A_{ji}	−2.2513	1.5898	−2.3657
D_{ij}	9.3990	0.3987	2.1415
D_{ji}	1.0619	0.8301	1.2131
E_{ij}	15.6929	0.0	7.9875
E_{ji}	6.9028	0.0	−0.2473

[a] Species listed in order i,j.

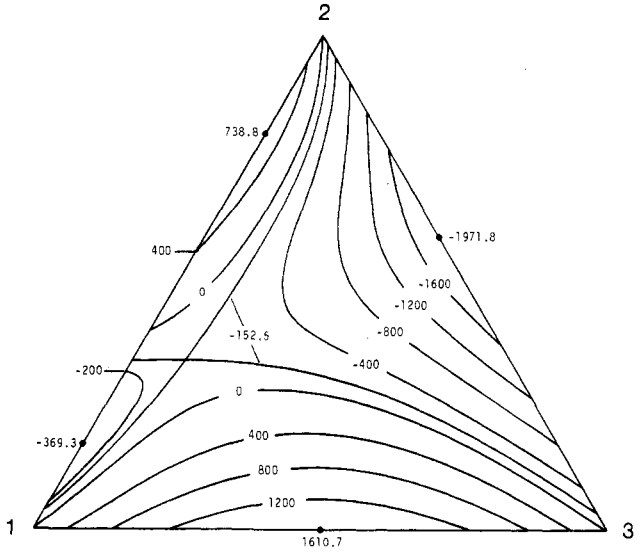

Figure 1. Lines of constant H^E (J mol^{-1}) for the ethanol (1)/chloroform (2)/1,4-dioxane (3) system at 50 °C.

Figures 1 and 2 provide pictorial representation of our results through contour diagrams of the H^E and TS^E surfaces.

Glossary

A_{ij}, A_{ji}	parameters in eq 1
C	function defined by eq 3
C_0, ..., C_5	parameters in eq 3
D_{ij}, D_{ji}	parameters in eq 1
E_{ij}, E_{ji}	parameters in eq 1
G^E	excess Gibbs energy

Table VI. Correlating Parameters in Eq 3 for Ethanol (1)/Chloroform (2)/1,4-Dioxane (3) at 50 °C

	$M^E_{123} \equiv H^E_{123}$	$M^E_{123} \equiv TS^E_{123}$
C_0	−0.3225	−1.1493
C_1	2.5187	3.7970
C_2	−0.8790	1.0319
C_3	−4.2648	−4.2648
C_4	−8.0475	−8.0475
C_5	−15.9696	−15.9696
σ, J mol^{-1}	6.7	
max dev, J mol^{-1}	14.7	

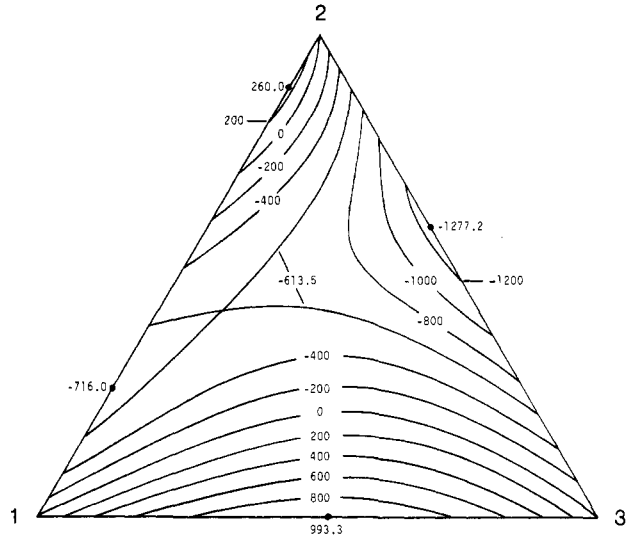

Figure 2. Lines of constant TS^E (J mol^{-1}) for the ethanol (1)/chloroform (2)/1,4-dioxane (3) system at 50 °C.

H^E	excess enthalpy
M^E	excess thermodynamic function
R	universal gas constant
S^E	excess entropy
T	absolute temperature
x_i, x_j	mole fraction

Greek Letters

σ	standard deviation

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

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