Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of 1-Chlorobutane with Ethyl Acetate, Acetonitrile, Nitromethane, and Acetone

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Total-pressure vapor–liquid equilibrium (VLE) data are reported at approximately 298, 348, and 398 K for each of four 1-chlorobutane binaries with ethyl acetate, acetonitrile, nitromethane, and acetone as the other component. The experimental PTx data were reduced to y_i, γ_i, and G^E values by both the Mixon–Gumowski–Carpenter and the Barker methods; the Mixon et al. results were deemed better and are reported. Six G^E correlations were tested in the Barker data reduction; the five-constant Redlich–Kister equation gave the best results. Various equations of state were used to estimate the vapor-phase fugacity coefficients; the Peng–Robinson results were used for the values reported.

Introduction

The data for the four systems covered in this paper were measured as part of a long-range effort to expand the vapor–liquid equilibrium (VLE) data base for a general correlation of mixture properties. Data were measured at three temperatures for each system. Maher and Smith (*1*, *2*) have reported similar data previously for binary systems containing chlorobenzene and aniline, and Muthu et al. (*3*) have reported similar data for some systems containing nitriles. This paper presents data on four systems containing 1-chlorobutane plus a non-hydrocarbon compound.

The apparatus and techniques for the experimental measurements have been described in detail in a previous paper by Maher and Smith (*4*), along with the defining equation for the activity coefficient and the standard states used.

Chemicals Used

Table I lists the chemicals used and their stated purity. All chemicals were available in at least 99.9% purity. Activated molecular sieves (either 3A or 4A) were put into the containers with the chemicals as they were received. Prior to being loaded into the VLE cells, the chemicals were poured into 500-mL flasks and then distilled through a Vigreux column (25-mm o.d. and 470 mm long). The first and last portions of the distillate were discarded. The retained samples were back-flushed with nitrogen and put into amber glass bottles for transfer to the loading operation. The initial purity of the chemicals was verified chromatographically. None of the compounds exhibited any degradation during the VLE measurements; the cell pressures were stable with respect to time, and all liquids were still perfectly clear when removed from the cells at the end of the last isotherm.

Experimental Data

Table I. Chemicals Used

component	vendor	stated purity, %
1-chlorobutane	Burdick and Jackson	99.9+
ethyl acetate	Burdick and Jackson	99.9
acetonitrile	Burdick and Jackson	99.9+
nitromethane	Mallinckrodt	99.9
acetone	Burdick and Jackson	99.9+

The experimental PTx data measured for the four systems are given in Tables II–V. The "smooth" pressure values reported there are from the least-squares cubic splined fits used to interpolate the experimental P vs. x_1 values to provide the evenly spaced values required by the finite-difference Mixon–Gumowski–Carpenter method (*5*).

The experimental data are plotted in Figures 1–4 in terms of the deviation pressure P_D which is the deviation from Raoult's law:

$$P_D = P - [P_2' + x_1(P_1' - P_2')]$$

where P is the experimental mixture pressure and the P_i' values are the pure-component vapor pressures. The deviation pressure plot emphasizes the scatter in the data more than a P vs. x_1 plot but has the disadvantage of not making obvious the existence of an azeotrope if one exists. All four systems showed positive deviations from Raoult's law (P_D values were positive) at all temperatures over the entire composition range.

An inspection of the pressure values in Tables II–V shows that ethyl acetate, acetonitrile, and nitromethane all formed azeotropes with 1-chlorobutane at all three temperatures studied. The acetone + 1-chlorobutane system did not form an azeotrope at any of the three temperatures.

Reduced Data

The y_i, γ_i, and G^E values selected for publication are in Tables VI–IX. Those values were obtained with the Mixon et al. data reduction method, using the Peng–Robinson equation of state (*6*) to estimate the vapor-phase fugacity coefficients. The "experimental" pressure values tabulated in Tables VI–IX are actually interpolated values from the cubic splined fits of the experimental P vs. x_1 values. (The fidelity with which the splined fits represent the actual experimental P values is shown in Tables II–V.) The "calculated" pressure values are from the Mixon et al. data reduction and show how well that method reproduces the original pressure data.

The calculated activity coefficient curves are shown in Figures 5–8 for both the Mixon et al. and the Barker (*7*) data reduction methods. The Barker calculation used the five-constant Redlich–Kister equation for G^E. The Peng–Robinson equation of state was used for both sets of results shown. The points are the evenly spaced Mixon et al. values while the curves represent the Barker-method results. The results from the two methods agree exceptionally well for the four systems covered in this paper.

Comparison of Data Reduction Procedures

The calculated P, y_i, γ_i, and G^E values obtained from the experimental PTx data are affected by three choices made in

0021-9568/83/1728-0086$01.50/0

Table II. Experimental P vs. x_1 Values for the Ethyl Acetate (1) + 1-Chlorobutane (2) System

298.15 K			348.16 K			398.18 K		
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	13.602	13.600	.0000	91.05	91.05	.0000	353.8	353.9
.0410	13.703	13.710	.0410	92.14	92.13	.0409	358.5	358.5
.0832	13.807	13.803	.0832	93.07	93.08	.0831	362.7	362.7
.1468	13.914	13.911	.1467	94.27	94.27	.1466	368.4	368.4
.2173	13.998	13.996	.2172	95.39	95.37	.2171	374.0	374.0
.3059	14.049	14.057	.3058	96.47	96.48	.3057	380.2	380.2
.4026	14.067	14.064	.4025	97.35	97.35	.4024	385.7	385.7
.5079	14.010	14.004	.5078	97.92	97.90	.5077	390.3	390.4
.6023	13.882	13.890	.6023	98.03	98.05	.6022	393.4	393.4
.7004	13.709	13.708	.7004	97.86	97.84	.7004	395.4	395.4
.7847	13.502	13.496	.7847	97.39	97.39	.7847	396.2	396.2
.8393	13.326	13.331	.8393	96.93	96.94	.8393	396.2	396.3
.9101	13.074	13.075	.9101	96.18	96.18	.9101	395.7	395.7
.9545	12.878	12.877	.9545	95.56	95.55	.9545	394.9	394.9
1.0000	12.630	12.630	1.0000	94.73	94.74	1.0000	393.6	393.6

Table III. Experimental P vs. x_1 Values for the 1-Chlorobutane (1) + Acetonitrile (2) System

298.69 K			348.18 K			398.89 K		
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	12.143	12.143	.0000	82.25	82.26	.0000	343.5	343.5
.0492	14.274	14.281	.0491	92.64	92.63	.0490	374.5	374.4
.0784	15.130	15.114	.0784	97.14	97.15	.0782	388.5	388.6
.1347	16.316	16.330	.1346	103.54	103.53	.1344	409.5	409.6
.2041	17.308	17.320	.2040	108.97	109.06	.2038	428.1	428.2
.2700	17.878	17.864	.2698	112.76	112.57	.2697	440.9	440.3
.3826	18.264	18.270	.3825	115.38	115.58	.3824	450.2	450.9
.4878	18.423	18.434	.4878	116.41	116.33	.4878	453.1	453.0
.5855	18.412	18.431	.5855	116.33	116.27	.5856	451.6	451.1
.6895	18.208	18.197	.6897	114.85	114.92	.6899	443.3	443.8
.7800	17.770	17.749	.7801	111.96	111.97	.7805	432.1	431.6
.8383	17.273	17.289	.8385	108.95	108.90	.8390	419.7	420.0
.9147	16.215	16.230	.9148	102.82	102.88	.9152	398.0	393.0
.9592	15.255	15.234	.9593	97.69	97.65	.9595	380.5	380.3
1.0000	13.988	13.996	1.0000	91.28	91.29	1.0000	360.0	360.2

Table IV. Experimental P vs. x_1 Values for the 1-Chlorobutane (1) + Nitromethane (2) System

298.18 K			348.16 K			398.16 K		
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	4.784	4.784	.0000	42.17	42.17	.0000	200.79	200.79
.0409	7.566	7.567	.0408	54.87	54.87	.0407	237.21	237.20
.0844	9.455	9.452	.0843	64.36	64.37	.0841	265.85	265.86
.1399	10.870	10.876	.1397	72.64	72.61	.1395	292.5	292.6
.2091	11.930	11.924	.2089	79.39	79.42	.2086	316.0	315.9
.2942	12.638	12.641	.2940	84.76	84.73	.2936	336.5	336.5
.3915	13.169	13.169	.3912	88.91	88.92	.3910	352.7	352.9
.4942	13.562	13.563	.4941	92.03	92.05	.4939	364.7	364.6
.5860	13.841	13.838	.5858	94.09	94.08	.5857	372.0	372.1
.6792	14.082	14.086	.6791	95.63	95.63	.6791	376.9	376.9
.7773	14.265	14.264	.7773	96.44	96.43	.7773	378.0	377.9
.8334	14.300	14.298	.8334	96.33	96.34	.8335	376.2	376.2
.9056	14.217	14.218	.9056	95.32	95.34	.9057	370.7	370.7
.9572	13.999	13.999	.9572	93.64	93.62	.9573	363.6	363.5
1.0000	13.665	13.665	1.0000	91.28	91.29	1.0000	354.4	354.4

Table V. Experimental P vs. x_1 Values for the Acetone (1) + 1-Chlorobutane (2) System

298.16 K			348.16 K			398.17 K		
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	13.665	13.664	.0000	91.18	91.18	.0000	354.4	354.4
.0507	15.467	15.473	.0506	100.40	100.39	.0504	382.8	382.7
.1032	17.134	17.128	.1030	108.88	108.90	.1027	409.3	409.4
.1741	19.085	19.089	.1737	119.14	119.15	.1730	442.2	442.2
.2266	20.384	20.376	.2263	126.11	126.05	.2258	464.9	465.0
.3397	22.762	22.769	.3394	139.19	139.22	.3390	509.7	509.5
.4148	24.111	24.116	.4145	146.80	146.85	.4141	535.9	535.9
.5084	25.604	25.591	.5081	155.41	155.35	.5077	565.9	566.0
.6041	26.921	26.925	.6038	163.07	163.07	.6034	593.8	593.9
.6987	28.09	28.10	.6986	169.85	169.88	.6983	618.7	618.7
.7849	29.04	29.04	.7847	175.44	175.42	.7845	639.3	639.2
.8587	29.78	29.77	.8586	179.79	179.74	.8585	655.3	655.2
.9112	30.22	30.23	.9112	182.44	182.54	.9111	665.5	665.7
.9564	30.59	30.58	.9564	184.74	184.66	.9563	674.0	673.8
1.0000	30.85	30.85	1.0000	186.31	186.33	1.0000	680.2	680.3

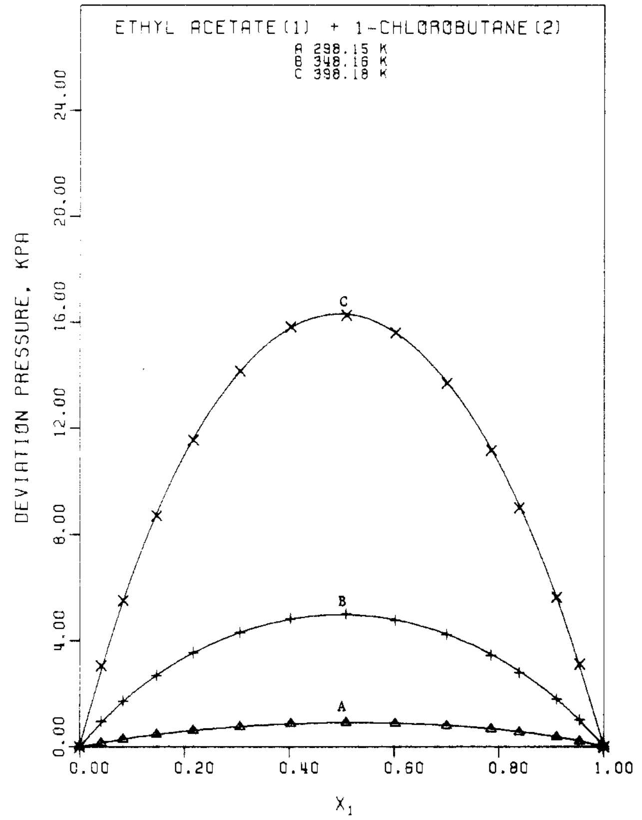

Figure 1. Deviation from Raoult's law for the ethyl acetate (1) + 1-chlorobutane (2) system.

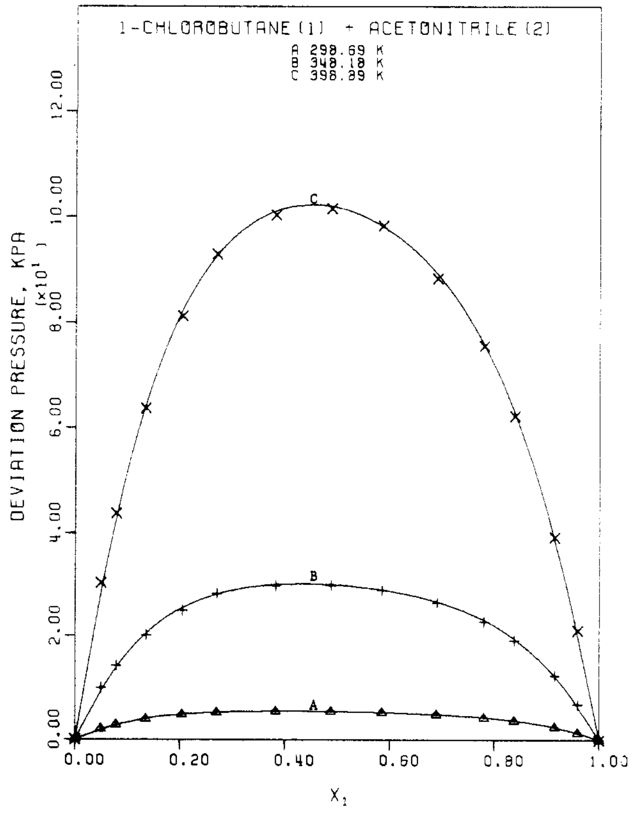

Figure 2. Deviation from Raoult's law for the 1-chlorobutane (1) + acetonitrile (2) system. The 10^1 multiplier on the ordinate scale means that the ordinate values run from 0.0 to 120.0.

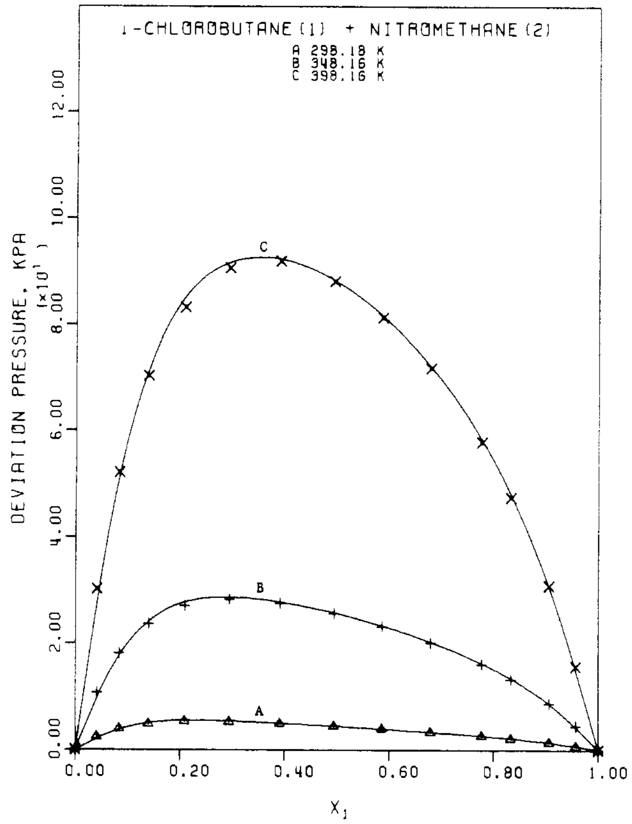

Figure 3. Deviation from Raoult's law for the 1-chlorobutane (1) + nitromethane (2) system. The 10^1 multiplier on the ordinate scale means that the ordinate values run from 0.0 to 120.0.

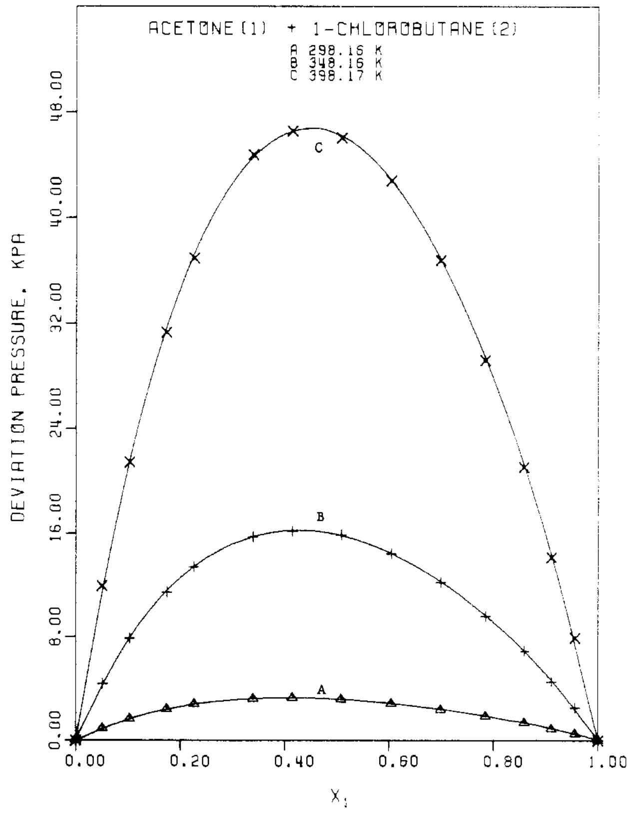

Figure 4. Deviation from Raoult's law for the acetone (1) + 1-chlorobutane (2) system.

Table VI. Calculated Data for the Ethyl Acetate (1) + 1-Chlorobutane (2) System at 298.15, 348.16, and 398.18 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 98.361 VL(2) = 105.120

X1	TOTAL PRESSURE, KPA EXPTL.	TOTAL PRESSURE, KPA CALC.	MIXTURE FUGACITY COEFFICIENTS 1	MIXTURE FUGACITY COEFFICIENTS 2	Y1	ACTIVITY COEFFICIENTS 1	ACTIVITY COEFFICIENTS 2	EXCESS GIBBS FUNCTION, J/MOLE
.0000	13.600	13.600	.9930	.9928	.0000	1.3093	1.0000	0.00
.1000	13.835	13.835	.9929	.9926	.1124	1.2304	1.0032	58.43
.2000	13.978	13.979	.9929	.9926	.2134	1.1798	1.0105	102.65
.3000	14.054	14.054	.9928	.9925	.3071	1.1381	1.0227	135.19
.4000	14.065	14.065	.9928	.9925	.3957	1.1008	1.0413	155.39
.5000	14.011	14.011	.9928	.9925	.4826	1.0699	1.0658	162.74
.6000	13.893	13.893	.9929	.9926	.5706	1.0453	1.0965	157.30
.7000	13.709	13.708	.9930	.9927	.6627	1.0269	1.1333	139.10
.8000	13.452	13.452	.9931	.9928	.7622	1.0142	1.1763	108.52
.9000	13.115	13.115	.9933	.9930	.8710	1.0046	1.2442	64.49
1.0000	12.630	12.630	.9935	.9933	1.0000	1.0000	1.3632	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 105.860 VL(2) = 112.241

X1	TOTAL PRESSURE, KPA EXPTL.	TOTAL PRESSURE, KPA CALC.	MIXTURE FUGACITY COEFFICIENTS 1	MIXTURE FUGACITY COEFFICIENTS 2	Y1	ACTIVITY COEFFICIENTS 1	ACTIVITY COEFFICIENTS 2	EXCESS GIBBS FUNCTION, J/MOLE
.0000	91.055	91.055	.9696	.9676	.0000	1.2523	1.0000	0.00
.1000	93.415	93.415	.9688	.9668	.1191	1.1751	1.0032	54.97
.2000	95.119	95.122	.9682	.9662	.2257	1.1331	1.0094	94.02
.3000	96.421	96.425	.9677	.9657	.3252	1.1025	1.0187	122.25
.4000	97.337	97.341	.9674	.9654	.4190	1.0753	1.0325	139.63
.5000	97.876	97.880	.9672	.9652	.5097	1.0519	1.0513	145.61
.6000	98.046	98.050	.9672	.9652	.5996	1.0330	1.0748	139.95
.7000	97.846	97.850	.9673	.9652	.6913	1.0188	1.1027	122.72
.8000	97.273	97.275	.9674	.9654	.7872	1.0094	1.1339	94.36
.9000	96.310	96.309	.9678	.9658	.8885	1.0030	1.1766	54.98
1.0000	94.737	94.737	.9683	.9664	1.0000	1.0000	1.2496	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 115.440 VL(2) = 121.150

X1	TOTAL PRESSURE, KPA EXPTL.	TOTAL PRESSURE, KPA CALC.	MIXTURE FUGACITY COEFFICIENTS 1	MIXTURE FUGACITY COEFFICIENTS 2	Y1	ACTIVITY COEFFICIENTS 1	ACTIVITY COEFFICIENTS 2	EXCESS GIBBS FUNCTION, J/MOLE
.0000	353.861	353.861	.9198	.9127	.0000	1.1811	1.0000	0.00
.1000	364.299	364.303	.9174	.9102	.1211	1.1298	1.0022	47.03
.2000	372.726	372.734	.9154	.9081	.2308	1.0995	1.0069	81.04
.3000	379.791	379.800	.9138	.9064	.3334	1.0766	1.0140	105.55
.4000	385.557	385.568	.9125	.9050	.4304	1.0565	1.0244	120.62
.5000	390.065	390.075	.9115	.9039	.5239	1.0393	1.0382	125.94
.6000	393.338	393.347	.9107	.9031	.6155	1.0252	1.0557	121.26
.7000	395.400	395.408	.9102	.9027	.7073	1.0145	1.0764	106.57
.8000	396.272	396.278	.9100	.9025	.8010	1.0072	1.0999	82.18
.9000	395.839	395.841	.9101	.9026	.8974	1.0021	1.1331	47.58
1.0000	393.637	393.637	.9106	.9032	1.0000	1.0000	1.1800	0.00

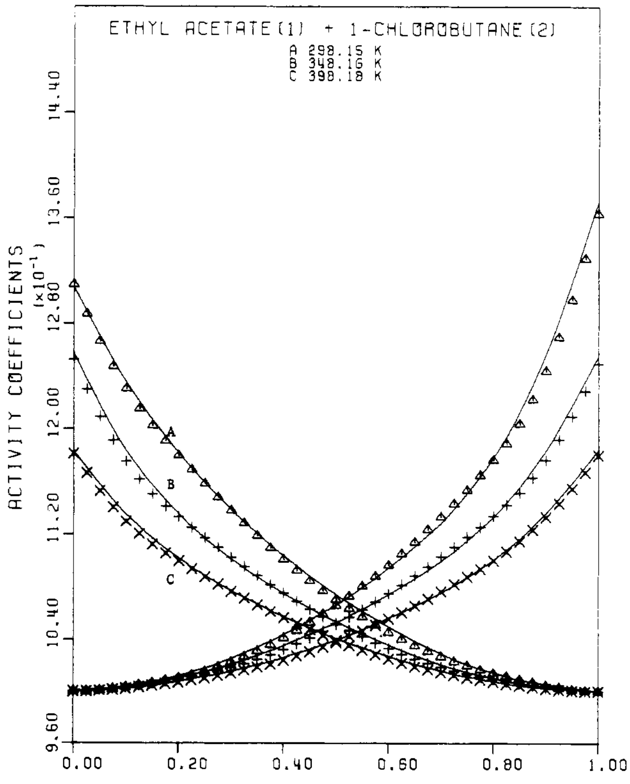

Figure 5. Activity coefficients for the ethyl acetate (1) + 1-chlorobutane (2) system. The curves represent the Barker values and the points are from the Mixon et al. method. The 10^{-1} multiplier means that the ordinate values run from 0.960 to 1.440.

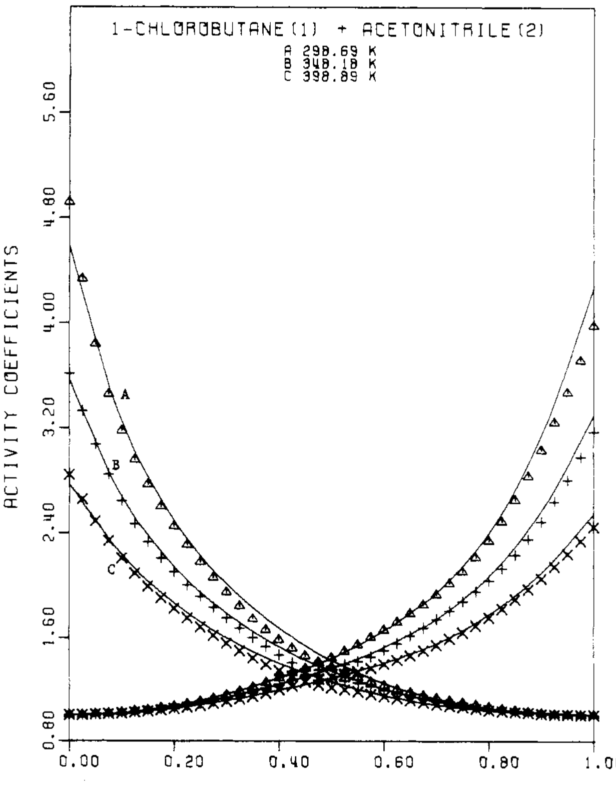

Figure 6. Activity coefficients for the 1-chlorobutane (1) + acetonitrile (2) system. The curves represent the Barker results and the points are from the Mixon et al. method.

Table VII. Calculated Data for the 1-Chlorobutane (1) + Acetonitrile (2) System at 298.69, 348.18, and 398.89 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 105.194 VL(2) = 52.859

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	12.143	12.143	.9936	.9946	.0000	4.9178	1.0000	0.00
.1000	15.629	15.628	.9918	.9931	.2846	3.1755	1.0214	334.18
.2000	17.274	17.274	.9909	.9923	.3974	2.4477	1.0690	577.13
.3000	18.019	18.019	.9905	.9920	.4537	1.9428	1.1548	745.05
.4000	18.306	18.306	.9903	.9919	.4858	1.5847	1.2882	834.75
.5000	18.443	18.443	.9903	.9918	.5217	1.3714	1.4487	852.42
.6000	18.414	18.414	.9903	.9918	.5611	1.2273	1.6590	808.07
.7000	18.158	18.158	.9904	.9920	.6123	1.1322	1.9272	704.55
.8000	17.613	17.613	.9907	.9922	.6767	1.0622	2.3391	541.92
.9000	16.489	16.489	.9913	.9927	.7763	1.0148	3.0314	308.15
1.0000	13.996	13.996	.9926	.9938	1.0000	1.0000	3.9829	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 112.244 VL(2) = 56.417

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	82.257	82.257	.9710	.9757	.0000	3.6180	1.0000	0.00
.1000	99.900	99.898	.9647	.9705	.2424	2.6441	1.0165	324.12
.2000	108.798	108.798	.9615	.9679	.3547	2.0989	1.0579	559.52
.3000	113.701	113.701	.9597	.9665	.4247	1.7473	1.1247	722.80
.4000	115.798	115.800	.9590	.9659	.4678	1.4689	1.2354	812.40
.5000	116.361	116.364	.9588	.9658	.5073	1.2803	1.3788	822.62
.6000	116.182	116.184	.9588	.9659	.5694	1.1958	1.5040	783.16
.7000	114.678	114.681	.9593	.9663	.6222	1.1060	1.7378	684.20
.8000	111.037	111.040	.9606	.9674	.6955	1.0491	2.0363	522.73
.9000	104.299	104.300	.9630	.9695	.8022	1.0130	2.4911	297.80
1.0000	91.292	91.292	.9676	.9734	1.0000	1.0000	3.1799	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 121.419 VL(2) = 61.001

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	343.523	343.523	.9166	.9307	.0000	2.8467	1.0000	0.00
.1000	397.571	397.574	.9033	.9199	.2019	2.2057	1.0133	301.92
.2000	427.403	427.409	.8959	.9140	.3130	1.8206	1.0477	520.96
.3000	444.214	444.215	.8917	.9107	.3880	1.5555	1.1042	669.68
.4000	451.633	451.630	.8898	.9093	.4407	1.3439	1.1949	746.57
.5000	452.994	452.985	.8894	.9091	.4960	1.2130	1.2958	749.90
.6000	450.426	450.411	.8899	.9097	.5642	1.1441	1.3935	708.19
.7000	442.740	442.726	.8917	.9114	.6323	1.0828	1.5440	616.82
.8000	428.163	428.161	.8952	.9144	.7135	1.0385	1.7513	472.00
.9000	403.166	403.167	.9012	.9196	.8224	1.0095	2.0573	267.58
1.0000	360.174	360.174	.9116	.9284	1.0000	1.0000	2.4605	0.00

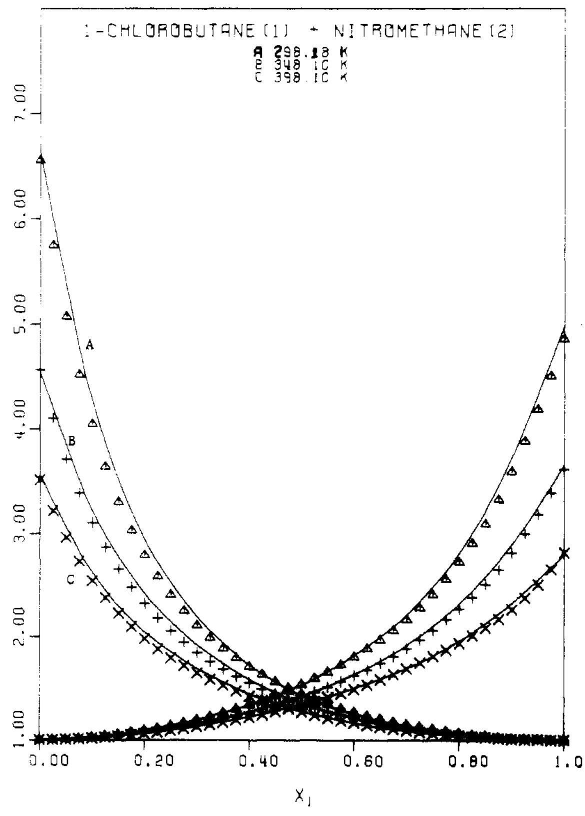

Figure 7. Activity coefficients for the 1-chlorobutane (1) + nitromethane (2) system. The curves represent the Barker results and the points are from the Mixon et al. method.

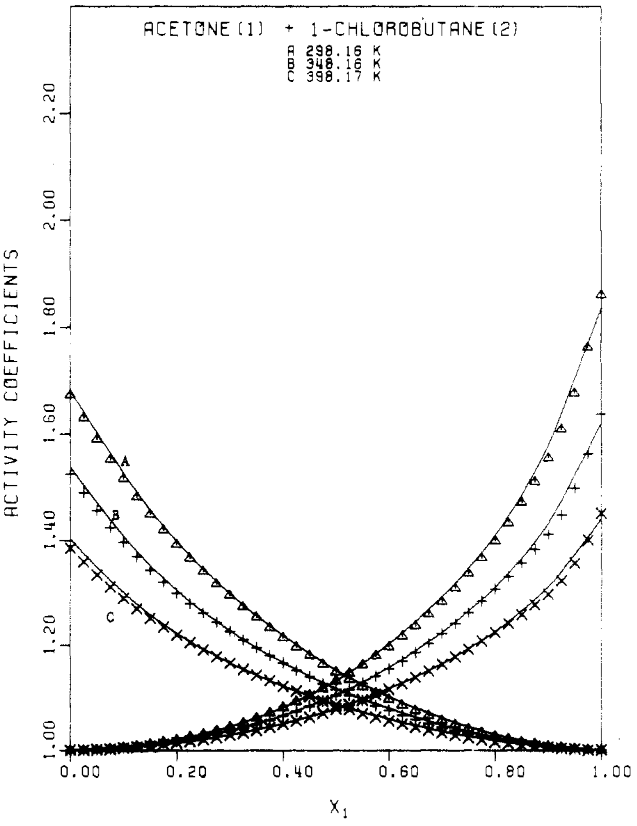

Figure 8. Activity coefficients for the acetone (1) + 1-chlorobutane (2) system. The curves represent the Barker results and the points are from the Mixon et al. method.

Table VIII. Calculated Data for the 1-Chlorobutane (1) + Nitromethane (2) System at 298.18, 348.16, and 398.16 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 105.128 VL(2) = 53.990

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	4.784	4.784	.9975	.9980	.0000	6.5532	1.0000	0.00
.1000	9.938	9.937	.9947	.9959	.5549	4.0441	1.0251	401.66
.2000	11.816	11.816	.9937	.9951	.6449	2.7911	1.0932	685.74
.3000	12.678	12.678	.9933	.9948	.6822	2.1108	1.1992	870.94
.4000	13.207	13.207	.9930	.9945	.7071	1.7090	1.3429	970.06
.5000	13.581	13.581	.9928	.9944	.7281	1.4474	1.5382	992.11
.6000	13.878	13.878	.9926	.9943	.7502	1.2696	1.8048	940.64
.7000	14.134	14.134	.9925	.9942	.7793	1.1512	2.1647	818.78
.8000	14.285	14.285	.9924	.9941	.8168	1.0670	2.7237	625.50
.9000	14.232	14.232	.9924	.9942	.8786	1.0164	3.5971	353.72
1.0000	13.665	13.665	.9927	.9944	1.0000	1.0000	4.8616	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 112.241 VL(2) = 57.390

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	42.168	42.168	.9852	.9883	.0000	4.5645	1.0000	0.00
.1000	67.075	67.073	.9763	.9815	.4187	3.1072	1.0197	379.05
.2000	78.700	78.700	.9721	.9783	.5350	2.3181	1.0731	650.14
.3000	85.032	85.032	.9699	.9766	.5932	1.8466	1.1571	828.32
.4000	89.236	89.237	.9683	.9755	.6350	1.5531	1.2696	924.40
.5000	92.198	92.193	.9673	.9747	.6702	1.3534	1.4208	946.35
.6000	94.347	94.347	.9665	.9742	.7053	1.2134	1.6232	896.85
.7000	95.890	95.890	.9660	.9738	.7471	1.1191	1.8865	779.19
.8000	96.452	96.452	.9657	.9737	.7981	1.0519	2.2722	592.32
.9000	95.469	95.469	.9661	.9740	.8736	1.0134	2.8167	334.54
1.0000	91.289	91.289	.9675	.9753	1.0000	1.0000	3.6146	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 121.266 VL(2) = 61.450

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	200.791	200.791	.9512	.9615	.0000	3.5153	1.0000	0.00
.1000	274.505	274.499	.9328	.9475	.3198	2.5395	1.0168	358.17
.2000	313.407	313.407	.9231	.9403	.4423	1.9814	1.0618	611.65
.3000	337.783	337.785	.9171	.9358	.5165	1.6499	1.1281	776.63
.4000	354.072	354.073	.9130	.9328	.5710	1.4269	1.2197	865.25
.5000	365.133	365.133	.9102	.9308	.6176	1.2689	1.3423	881.41
.6000	373.072	373.072	.9082	.9295	.6666	1.1631	1.4925	830.36
.7000	377.491	377.491	.9071	.9288	.7199	1.0879	1.6902	716.46
.8000	377.467	377.466	.9070	.9290	.7861	1.0394	1.9359	539.67
.9000	371.308	371.307	.9085	.9304	.8729	1.0110	2.2664	303.53
1.0000	354.394	354.394	.9126	.9340	1.0000	1.0000	2.8149	0.00

the data reduction: (1) the data reduction method used—direct (Mixon et al.) or indirect (Barker), (2) the choice of the G^E equation used in the indirect method, and (3) the equation of state used to estimate the vapor-phase fugacity coefficients. As new data are measured in the Thermodynamics Research Laboratory, the effects of those three choices on the results obtained are being systematically investigated. Some of the results from that work are summarized below.

The four systems covered in this paper are all well-behaved—there are no mixed deviation systems and the level of nonideality changes monotonically with temperature in all cases. As a result, the disagreements between the various data reduction procedures are not as sharp as for less well-behaved systems. The disagreements were greatest for the highest-temperature data for the 1-chlorobutane (1) + acetonitrile (2) system at 398.89 K, and that set will be used for the comparisons. Also, the infinite-dilution values will be used for the comparisons because they are the most sensitive to the procedures used.

Table X compares three methods of obtaining γ_i^∞ values. The third method shown—the Gautreaux–Coates equations (*8*)—requires $(dP/dx_1)_i^\infty$ values, and the use of P_D/x_1x_2 or x_1x_2/P_D vs. x_1 plots to obtain those values has been discussed by Maher and Smith (*9*). The $(dP/dx_1)_i^\infty$ values can also be obtained from the cubic splined fits used to interpolate the experimental P vs. x_1 data to provide the evenly spaced P vs. x_1 values required by the Mixon et al. method.

When the Mixon et al. and Barker methods give widely different values for γ_1^∞ and γ_2^∞, the Gautreaux–Coates values will sometimes help decide which set is better. Unfortunately, there is always some uncertainty (sometimes small and sometimes very large) in the extrapolation of the experimental P_D/x_1x_2 or x_1x_2/P_D plots to $x_1 = 0.0$ and 1.0. Also, one would expect the Gautreaux–Coates values obtained when the splined-fit $(dP/dx_1)_i^\infty$ values are used to agree better with the Mixon et al. values than with the Barker results.

In the choice of the better data reduction method, the most weight must be given to how well the various procedures reproduce the experimental P vs. x_1 isotherm. The numbers in parentheses in Table X show the worst percentage deviation followed by the root-mean-squared percentage deviation. (Those deviations are defined at the bottom of Table XII.) Of the various G^E correlations used in the indirect Barker method, the five-constant Redlich–Kister equation almost invariably gives the smallest pressure deviations with the five-constant modified Margules equation of Abbott and Van Ness (*10*) usually a close second. No restrictions were placed on the α in the NRTL equation; hence, it was used as a three-constant equation. All the others had two adjustable constants.

The Barker results for γ_1^∞ in Table X vary from 2.398 to 2.697, which is an 18.8% variation in the level of nonideality predicted. The base for this percentage is the Mixon et al.

Table IX. Calculated Data for the Acetone (1) + Chlorobutane (2) System at 298.16, 348.16, and 398.17 K

```
 LIQUID MOLAR VOLUMES, CC/MOL: VL(1) =   74.035  VL(2) =  105.125

                                                                                 EXCESS
                                    MIXTURE FUGACITY                              GIBBS
          IOTAL PRESSURE, KPA        COEFFICIENTS                 ACTIVITY COEFFICIENTS         FUNCTION,
  X1       EXPIL.        CALC.         1        2         Y1          1           2           J/MOLE
 .0000     13.664       13.664       .9951    .9927      .0000      1.6729      1.0000          0.00
 .1000     17.034       17.034       .9938    .9910      .2729      1.5158      1.0052        114.67
 .2000     19.740       19.741       .9927    .9896      .4330      1.3920      1.0203        203.93
 .3000     21.983       21.984       .9919    .9884      .5431      1.2948      1.0453        268.98
 .4000     23.862       23.863       .9911    .9874      .6261      1.2143      1.0821        309.87
 .5000     25.466       25.466       .9905    .9866      .6942      1.1486      1.1324        325.94
 .6000     26.872       26.872       .9900    .9859      .7546      1.0974      1.1975        316.93
 .7000     28.110       28.110       .9895    .9853      .8114      1.0574      1.2832        282.30
 .8000     29.195       29.195       .9891    .9848      .8679      1.0274      1.3995        220.22
 .9000     30.137       30.137       .9887    .9844      .9288      1.0085      1.5553        128.47
1.0000     30.848       30.848       .9885    .9841     1.0000      1.0000      1.8598          0.00

 LIQUID MOLAR VOLUMES, CC/MUL: VL(1) =   79.879  VL(2) =  112.241

                                                                                 EXCESS
                                    MIXTURE FUGACITY                              GIBBS
          IOTAL PRESSURE, KPA        COEFFICIENTS                 ACTIVITY COEFFICIENTS         FUNCTION,
  X1       EXPTL.        CALC.         1        2         Y1          1           2           J/MOLE
 .0000     91.180       91.180       .9787    .9676      .0000      1.5255      1.0000          0.00
 .1000    108.444      108.446       .9741    .9615      .2345      1.3960      1.0046        108.62
 .2000    122.669      122.672       .9704    .9566      .3874      1.2990      1.0174        191.28
 .3000    134.876      134.879       .9673    .9525      .5006      1.2261      1.0371        250.83
 .4000    145.435      145.438       .9646    .9490      .5904      1.1658      1.0657        288.11
 .5000    154.645      154.647       .9623    .9459      .6661      1.1158      1.1046        302.62
 .6000    162.779      162.779       .9602    .9433      .7337      1.0756      1.1554        293.79
 .7000    169.978      169.978       .9584    .9410      .7972      1.0439      1.2216        260.81
 .8000    176.347      176.346       .9568    .9390      .8603      1.0206      1.3071        202.33
 .9000    181.971      181.970       .9554    .9373      .9267      1.0068      1.4125        117.64
1.0000    186.330      186.330       .9544    .9361     1.0000      1.0000      1.6368          0.00

 LIQUID MOLAR VOLUMES, CC/MOL: VL(1) =   87.709  VL(2) =  121.266

                                                                                 EXCESS
                                    MIXTURE FUGACITY                              GIBBS
          TOTAL PRESSURE, KPA        COEFFICIENTS                 ACTIVITY COEFFICIENTS         FUNCTION,
  X1       EXPTL.        CALC.         1        2         Y1          1           2           J/MOLE
 .0000    354.430      354.430       .9442    .9126      .0000      1.3853      1.0000          0.00
 .1000    408.083      408.093       .9344    .8996      .2026      1.2895      1.0037         95.24
 .2000    454.032      454.044       .9261    .8888      .3477      1.2189      1.0136        166.87
 .3000    494.792      494.798       .9189    .8793      .4620      1.1662      1.0286        218.10
 .4000    531.138      531.138       .9125    .8711      .5567      1.1224      1.0500        249.94
 .5000    563.663      563.659       .9068    .8638      .6389      1.0859      1.0789        262.10
 .6000    592.908      592.903       .9017    .8574      .7135      1.0562      1.1161        254.10
 .7000    619.171      619.166       .8972    .8519      .7838      1.0327      1.1639        225.25
 .8000    642.673      642.670       .8932    .8470      .8530      1.0155      1.2241        174.57
 .9000    663.585      663.586       .8896    .8430      .9241      1.0052      1.2973        101.60
1.0000    680.294      680.294       .8868    .8400     1.0000      1.0000      1.4516          0.00
```

Table X. Effect of Calculation Method on γ_i^∞ Values for 1-Chlorobutane (1) + Acetonitrile (2) at 398.89 K[a]

calculation method	γ_i^∞ 1	γ_i^∞ 2
Mixon–Gumowski–Carpenter (0.16/0.08)[b]	2.593	2.417
Barker:		
"absolute" Van Laar (0.70/0.42)	2.398	2.230
Wilson (1.00/0.50)	2.549	2.183
NRTL (0.64/0.38)	2.401	2.329
modified Margules (0.26/0.15)	2.697	2.584
UNIQUAC (0.73/0.42)	2.412	2.227
Redlich–Kister, five constants (0.24/0.09)	2.520	2.453
Gautreaux–Coates:		
splined fits	2.593	2.417
P_D/x_1x_2 plot	2.619	2.438

[a] Virial equation through B_{ij}, Tsonopoulos correlation. [b] First number in parentheses is the maximum percent deviation in P. The second number is the root mean square of the percent deviation in P. See bottom of Table XII.

Table XI. Effect of Equation of State Choice on γ_i^∞ Values Obtained with Mixon et al. Method for 1-Chlorobutane (1) + Acetonitrile (2) at 398.89 K

eq of state used	γ_i^∞ 1	γ_i^∞ 2
ideal gas	2.982	2.620
virial through B_{ij}		
Pitzer–Curl	2.825	2.442
O'Connell–Prausnitz	2.791	2.714
Tsonopoulos	2.593	2.417
Nothnagel	2.893	2.582
Redlich–Kwong (unmodified)	2.870	2.482
Peng–Robinson	2.847	2.460

value of 2.593 − 1.0. (One should always subtract the ideal solution value of 1.0 when citing percentage errors in activity coefficient values.)

The effect of the equation of state used is illustrated in Table XI. The effect of the equation of state choice is not dramatic for these systems but nevertheless the results vary appreciably. On the basis of the comparisons shown, the Peng–Robinson equation is a reasonable choice for the final results presented in Tables VI–IX and Figures 5–8.

Table XII compares the Mixon et al. and the Barker methods in terms of how well they reproduce the experimental P vs. x_1 data for all four systems. The Barker results are from the five-constant Redlich–Kister equation for G^E, and the Peng–Robinson equation of state was used for both methods. As can be seen from Table XII, both methods work well for the four systems covered in this paper with the Mixon et al. method showing a clear advantage only for the 1-chlorobutane + acetonitrile system.

On the basis of the kinds of results illustrated in Tables X–

XII, the results obtained with the Mixon et al. procedure plus the Peng–Robinson equation of state were chosen for presentation in Tables VI–IX and Figures 5–8. Table XIII lists the compound constants used for the Peng–Robinson equation.

Registry No. 1-Chlorobutane, 109-69-3; ethyl acetate, 141-78-6; acetonitrile, 75-05-8; acetone, 67-64-1; nitromethane, 75-52-5.

Table XII. Comparison of the Barker and Mixon et al. Pressure Fits

	max % dev in P[a]		rms for % dev[b]	
temp, K	Barker	Mixon	Barker	Mixon
Ethyl Acetate (1) + 1-Chlorobutane (2)				
298.15	0.055	0.055	0.033	0.033
348.16	0.018	0.018	0.010	0.011
398.18	0.022	0.019	0.008	0.009
1-Chlorobutane (1) + Acetonitrile (2)				
298.69	0.332	0.139	0.158	0.085
348.18	0.386	0.169	0.133	0.074
398.89	0.276	0.156	0.109	0.083
1-Chlorobutane (1) + Nitromethane (2)				
298.18	0.160	0.059	0.071	0.025
348.16	0.036	0.047	0.019	0.023
398.16	0.037	0.049	0.020	0.020
Acetone (1) + 1-Chlorobutane (2)				
298.16	0.049	0.053	0.029	0.030
348.16	0.068	0.060	0.033	0.029
398.17	0.048	0.038	0.018	0.020

[a] % dev = $100[|P_{\text{calcd}} - P_{\text{exptl}}|/P_{\text{exptl}}]$. [b] rms for % dev = $[\Sigma^n(\%\ \text{dev})^2/n]^{1/2}$.

Table XIII. Compound Constants Used for the Peng-Robinson Equation of State[a]

compd	T_c, K	P_c, MPa	ω
1-chlorobutane	542.0	3.688	0.2180
ethyl acetate	523.2	3.830	0.3630
acetonitrile	548.0	4.833	0.3210
nitromethane	588.0	6.313	0.3460

[a] The binary interaction constant was set to 0.0 for all three binaries.

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Received for review July 16, 1982. Accepted September 24, 1982. We gratefully acknowledge the financial support received from the National Science Foundation Grant CPE-80000534 and from the Industrial Participants in the Thermodynamics Research Laboratory.

Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of 1-Chlorobutane with Pentane, Benzene, and Toluene

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Total-pressure vapor–liquid equilibrium (VLE) data are reported at approximately 298, 348, and 398 K for each of three chlorobutane binaries with pentane, benzene, and toluene as the other component. The experimental *PTx* data were reduced to y_i, γ_i, and G^E values by both the Mixon–Gumowski–Carpenter and the Barker methods, but only the Mixon et al. results are reported in their entirety. Seven G^E correlations were tested in the Barker data reduction; the five-constant Redlich–Kister equation gave the best results. Various equations of state were used to estimate the vapor-phase fugacity coefficients; the Peng–Robinson results were used for the values reported.

Introduction

This paper reports total-pressure (*PTx*) vapor–liquid equilibrium data for three systems containing 1-chlorobutane plus a hydrocarbon (pentane, benzene, and toluene). The apparatus and techniques for the experimental measurements have been described in detail in a previous paper (*1*), along with the defining equation for the activity coefficient and the standard states used.

Table I. Chemicals Used

component	vendor	stated purity %
1-chlorobutane	Burdick and Jackson	99.9+
pentane	Burdick and Jackson	99.9
benzene	Burdick and Jackson	99.9
toluene	Burdick and Jackson	99.9

Chemicals Used

The sources and purities of the chemicals used are listed in Table I. Activated molecular sieves (either 3A or 4A) were put into the chemical containers as they were received. Just prior to being loaded into the VLE cells, the chemicals were poured into distillation flasks and then distilled through a Vigreux column (25-mm o.d. and 470 mm long). The first and last portions of the distillate were discarded. The retained samples were back-flushed with dry nitrogen and put into amber glass bottles for transfer to the loading operation. The stated purities

0021-9568/83/1728-0093$01.50/0