Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of Chlorobenzene with Nitromethane, Ethanol, Benzene, and 1-Chlorobutane

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Total-pressure vapor–liquid equilibrium (VLE) data are reported at approximately 298, 348, and 398 K for each of four chlorobenzene binaries with nitromethane, ethanol, benzene, and 1-chlorobutane as the other components. 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. 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 vapor-phase fugacity coefficients. The Peng–Robinson equation of state was used for the reported data for the nitromethane and 1-chlorobutane systems. The virial equation through the second term, with the coefficients predicted by the Hayden–O'Connell correlation, was used for the data reported for the ethanol and benzene systems.

Introduction

This is the second paper reporting total-pressure vapor–liquid equilibrium (VLE) data on binary systems containing chlorobenzene. The first paper (*1*) used acetone, acetonitrile, ethyl acetate, ethylbenzene, methanol, and 1-pentene as the other component. This paper reports data for nitromethane, ethanol, benzene, and 1-chlorobutane.

The apparatus and techniques for the experimental measurements have been described in detail in a previous paper (*2*), along with the defining equation for the activity coefficient and the definition of the standard states used.

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 in the VLE cells, the chemicals were poured into distillation flasks and 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 cell-loading operation. The stated purities of the chemicals were verified chromatographically at this point.

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

Tables II–V present the experimental *PTx* data. The "smooth" pressure values reported there are from the least-squares cubic splined fits used to provide the evenly spaced values required by the finite-difference Mixon–Gumowski–Carpenter method (*3*) for reduction of *PTx* data.

Table I. Chemicals Used

component	vendor	stated purity, %
ethanol	U.S. Industrial Chemicals	200 proof
chlorobenzene	Burdick and Jackson	99.9+
1-chlorobutane	Burdick and Jackson	99.9+
benzene	Burdick and Jackson	99.9+

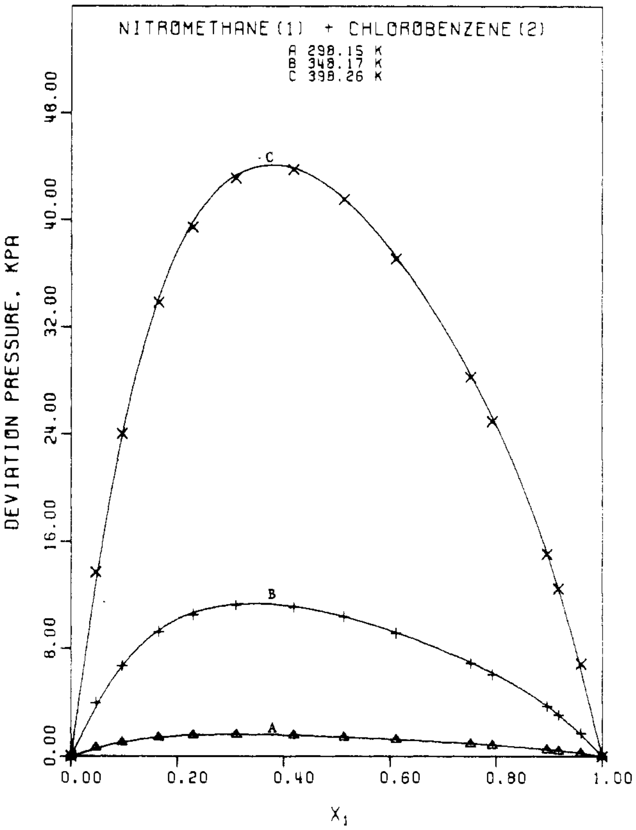

Figure 1. Deviation from Raoult's law for the nitromethane (1) + chlorobenzene (2) system.

Figures 1–4 show the experimental data in terms of the pressure deviation P_D 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 more than a P vs. x_1 plot but has the disadvantage of not indicating whether an azeotrope exists.

The point symbols in Figure 1–4 denote the experimental data points. The curves approximate—sometimes not very

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Table II. Experimental P vs. x_1 Values for the Nitromethane (1) + Chlorobenzene (2) System

298.15 K			348.17 K			398.26 K		
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	1.629	1.629	.0000	16.351	16.350	.0000	84.81	84.81
.0474	2.409	2.407	.0474	21.543	21.553	.0472	104.04	104.04
.0962	2.973	2.975	.0961	25.557	25.543	.0959	120.08	120.09
.1650	3.544	3.546	.1649	29.84	29.83	.1646	137.88	137.85
.2297	3.915	3.912	.2296	32.79	32.83	.2292	151.04	151.07
.3106	4.217	4.216	.3104	35.61	35.58	.3101	164.20	164.18
.4188	4.491	4.494	.4187	38.26	38.27	.4184	177.48	177.52
.5133	4.660	4.661	.5132	39.98	39.97	.5130	186.30	186.25
.6113	4.790	4.789	.6113	41.30	41.30	.6111	193.32	193.33
.7522	4.931	4.924	.7521	42.71	42.70	.7520	201.02	200.99
.7926	4.937	4.946	.7926	42.94	42.96	.7926	202.42	202.51
.8965	4.954	4.950	.8965	43.24	43.22	.8965	204.68	204.57
.9178	4.939	4.939	.9178	43.18	43.18	.9178	204.58	204.60
.9596	4.888	4.889	.9596	42.90	42.91	.9596	203.85	203.91
1.0000	4.782	4.782	1.0000	42.21	42.21	1.0000	201.73	201.71

Table III. Experimental P vs. x_1 Values for the Ethanol (1) + Chlorobenzene (2) System

298.15 K			348.35 K			398.66 K		
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	1.644	1.643	.0000	23.322	23.321	.0000	85.51	85.51
.0614	5.305	5.324	.0610	43.09	43.16	.0599	169.58	169.39
.0795	5.612	5.591	.0791	47.99	47.86	.0784	190.36	190.84
.1293	6.109	6.097	.1289	56.79	56.89	.1276	242.18	241.55
.1816	6.418	6.438	.1811	62.45	62.38	.1797	282.3	282.6
.2926	6.794	6.793	.2921	69.69	69.74	.2906	337.8	338.0
.3954	7.024	7.011	.3951	73.94	73.98	.3936	373.0	372.9
.4870	7.191	7.191	.4867	76.89	76.78	.4856	397.9	397.6
.5839	7.356	7.369	.5837	79.61	79.57	.5825	420.0	420.0
.6951	7.559	7.562	.6950	82.59	82.69	.6942	443.7	443.9
.7814	7.710	7.706	.7814	84.85	84.96	.7808	461.5	461.7
.8519	7.832	7.821	.8519	86.72	86.68	.8517	475.9	475.9
.9059	7.897	7.901	.9058	88.00	87.88	.9056	486.8	486.6
.9631	7.929	7.937	.9631	89.16	89.05	.9630	498.1	497.8
1.0000	7.914	7.910	1.0000	89.59	89.73	1.0000	504.7	505.0

Table IV. Experimental P vs. x_1 Values for the Benzene (1) + Chlorobenzene (2) System

298.20 K			348.16 K			398.66 K		
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	1.635	1.635	.0000	16.333	16.338	.0000	85.38	85.48
.0432	2.146	2.147	.0431	19.449	19.436	.0430	96.28	96.22
.0958	2.739	2.743	.0957	23.155	23.159	.0956	109.38	109.33
.1348	3.184	3.179	.1347	25.887	25.892	.1345	119.09	119.06
.1929	3.831	3.828	.1927	29.93	29.93	.1924	133.59	133.54
.2771	4.768	4.768	.2770	35.81	35.81	.2765	154.66	154.64
.3707	5.807	5.809	.3704	42.33	42.33	.3700	178.11	178.16
.4779	6.993	7.000	.4777	49.82	49.82	.4771	205.20	205.29
.5780	8.107	8.110	.5778	56.84	56.84	.5772	230.80	230.83
.6858	9.327	9.301	.6855	64.42	64.40	.6851	258.68	258.58
.7895	10.433	10.444	.7893	71.67	71.70	.7890	285.6	285.6
.8306	10.886	10.897	.8304	74.57	74.60	.8302	296.3	296.4
.9182	11.862	11.859	.9181	80.80	80.78	.9179	319.6	319.5
.9583	12.304	12.299	.9582	83.67	83.62	.9582	330.3	330.2
1.0000	12.755	12.757	1.0000	86.54	86.57	1.0000	341.3	341.4

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

298.17 K			348.17 K			398.21 K		
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	1.638	1.641	.0000	16.278	16.299	.0000	84.53	84.57
.0436	2.245	2.236	.0435	19.989	19.919	.0434	97.17	97.03
.0886	2.804	2.816	.0885	23.467	23.511	.0883	109.54	109.62
.1422	3.484	3.480	.1420	27.63	27.66	.1418	124.24	124.33
.2092	4.304	4.299	.2090	32.78	32.78	.2087	142.54	142.52
.2887	5.260	5.262	.2884	38.79	38.77	.2881	163.94	163.87
.3947	6.529	6.534	.3944	46.66	46.66	.3939	192.02	192.04
.4899	7.667	7.667	.4896	53.69	53.68	.4891	217.24	217.22
.5886	8.835	8.832	.5883	60.89	60.93	.5877	243.25	243.28
.6865	9.986	9.983	.6863	68.15	68.12	.6860	269.27	269.31
.8246	11.594	11.601	.8243	78.27	78.27	.8237	306.3	306.3
.8561	11.973	11.970	.8559	80.61	80.61	.8556	315.0	315.0
.9234	12.760	12.759	.9233	85.57	85.59	.9231	333.4	333.4
.9602	13.190	13.190	.9602	88.33	88.31	.9601	343.5	343.5
1.0000	13.654	13.654	1.0000	91.21	91.22	1.0000	354.4	354.4

Table VI. Calculated Data for the Nitromethane (1) + Chlorobenzene (2) System at 298.15, 348.17, and 398.26 K Obtained with the Mixon et al. Method and the Peng-Robinson Equation of State

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 53.942 VL(2) = 102.280

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	1.629	1.629	.9994	.9989	.0000	4.4135	1.0000	0.00
.1000	3.012	3.013	.9988	.9980	.5045	3.1809	1.0169	324.27
.2000	3.761	3.761	.9984	.9976	.6314	2.4843	1.0620	570.48
.3000	4.183	4.183	.9983	.9973	.6886	2.0083	1.1399	745.85
.4000	4.453	4.453	.9982	.9971	.7247	1.6875	1.2517	852.71
.5000	4.641	4.641	.9981	.9970	.7521	1.4598	1.4093	894.21
.6000	4.776	4.776	.9980	.9970	.7762	1.2920	1.6365	869.49
.7000	4.883	4.883	.9980	.9969	.8028	1.1710	1.9655	776.46
.8000	4.949	4.949	.9979	.9969	.8327	1.0771	2.5355	608.56
.9000	4.949	4.943	.9979	.9969	.8883	1.0213	3.3859	349.31
1.0000	4.782	4.782	.9980	.9970	1.0000	1.0000	5.1503	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 57.211 VL(2) = 107.691

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	16.350	16.350	.9958	.9928	.0000	3.4207	1.0000	0.00
.1000	25.321	25.322	.9930	.9887	.4193	2.5785	1.0144	311.54
.2000	31.562	31.564	.9914	.9863	.5613	2.1058	1.0510	546.46
.3000	35.273	35.274	.9903	.9847	.6358	1.7751	1.1126	714.51
.4000	37.872	37.872	.9896	.9836	.6859	1.5407	1.2006	818.03
.5000	39.760	39.760	.9890	.9829	.7246	1.3663	1.3247	858.80
.6000	41.163	41.162	.9886	.9823	.7588	1.2337	1.5010	835.11
.7000	42.263	42.262	.9883	.9819	.7947	1.1367	1.7482	744.79
.8000	42.996	42.995	.9861	.9816	.8351	1.0632	2.1412	582.70
.9000	43.212	43.212	.9880	.9816	.8967	1.0197	2.6979	338.12
1.0000	42.208	42.209	.9883	.9822	1.0000	1.0000	4.0137	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 61.120 VL(2) = 113.907

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	84.805	84.805	.9851	.9736	.0000	2.6586	1.0000	0.00
.1000	121.286	121.288	.9775	.9625	.3560	2.1798	1.0105	289.17
.2000	145.445	145.449	.9727	.9554	.5042	1.8413	1.0408	510.21
.3000	162.710	162.713	.9692	.9504	.5918	1.6054	1.0894	668.64
.4000	175.533	175.535	.9667	.9467	.6533	1.4298	1.1594	767.53
.5000	185.183	185.184	.9648	.9440	.7017	1.2934	1.2588	806.96
.6000	192.600	192.601	.9633	.9420	.7447	1.1877	1.3971	784.72
.7000	198.544	198.544	.9621	.9404	.7892	1.1106	1.5829	699.41
.8000	202.747	202.747	.9612	.9394	.8379	1.0525	1.8625	547.55
.9000	204.583	204.582	.9608	.9392	.9019	1.0158	2.2726	318.59
1.0000	201.714	201.714	.9613	.9407	1.0000	1.0000	3.1401	0.00

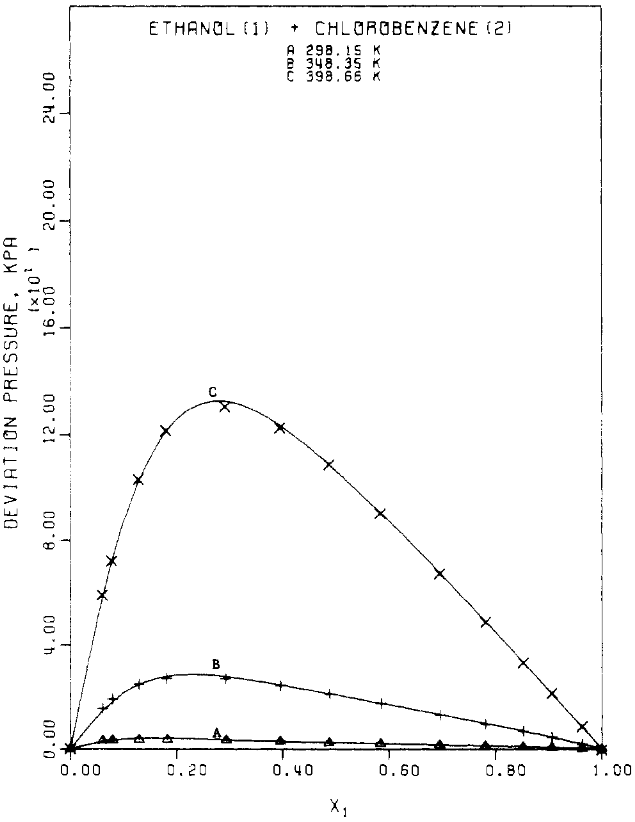

Figure 2. Deviation from Raoult's law for the ethanol (1) + chlorobenzene (2) system. Decimal point must be moved one place to right in ordinate scale values.

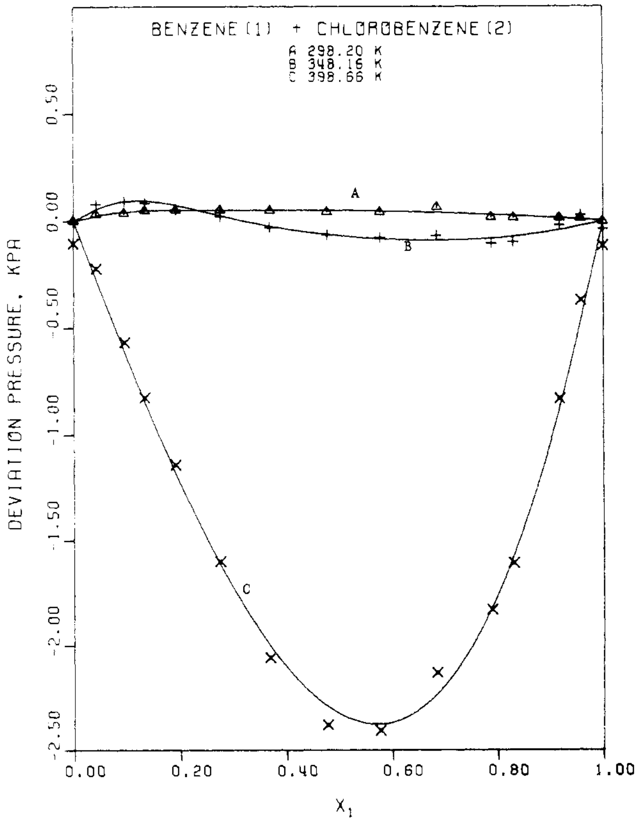

Figure 3. Deviation from Raoult's law for the benzene (1) + chlorobenzene (2) system.

Table VII. Calculated Data for the Ethanol (1) + Chlorobenzene (2) System at 298.15, 348.35, and 398.66 K Obtained with the Mixon et al. Method and the Virial Equation of State through B_{ij}

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 58.821 VL(2) = 102.280

VIRIAL COEFFICIENTS, CC/MOL: B(1,1) = -2169.9 B(1,2) = -1185.8 B(2,2) = -3127.6

X1	TOTAL PRESSURE, KPA EXPTL.	CALC.	MIXTURE FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	EXCESS GIBBS FUNCTION, J/MOLE
.0000	1.643	1.643	1.0005	.9979	.0000	15.6072	1.0000	0.00
.1000	5.825	5.824	.9954	.9963	.7317	5.4006	1.0545	536.46
.2000	6.523	6.523	.9947	.9963	.7668	3.1670	1.1549	857.09
.3000	6.809	6.809	.9944	.9963	.7810	2.2441	1.2938	1048.08
.4000	7.020	7.020	.9942	.9964	.7928	1.7610	1.4728	1136.98
.5000	7.216	7.216	.9940	.9964	.8054	1.4707	1.7059	1140.09
.6000	7.398	7.398	.9938	.9965	.8199	1.2789	2.0232	1064.71
.7000	7.570	7.570	.9936	.9967	.8384	1.1468	2.4779	912.55
.8000	7.736	7.736	.9934	.9971	.8663	1.0594	3.1425	682.14
.9000	7.893	7.893	.9932	.9979	.9187	1.0187	3.9024	378.84
1.0000	7.910	7.910	.9931	.9994	1.0000	1.0000	5.6941	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 63.708 VL(2) = 107.690

VIRIAL COEFFICIENTS, CC/MOL: B(1,1) = -976.6 B(1,2) = -785.8 B(2,2) = -1857.1

X1	TOTAL PRESSURE, KPA EXPTL.	CALC.	MIXTURE FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	EXCESS GIBBS FUNCTION, J/MOLE
.0000	23.321	23.321	1.0025	.9850	.0000	4.3344	1.0000	0.00
.1000	52.272	52.270	.9863	.9744	.5878	3.4852	1.0144	398.88
.2000	63.919	63.917	.9813	.9719	.6803	2.4535	1.0790	695.98
.3000	70.129	70.128	.9787	.9710	.7222	1.8999	1.1741	883.01
.4000	74.141	74.141	.9770	.9706	.7496	1.5607	1.3048	978.03
.5000	77.161	77.161	.9757	.9706	.7726	1.3373	1.4799	988.59
.6000	80.041	80.041	.9744	.9709	.7985	1.1932	1.7004	921.99
.7000	82.827	82.828	.9731	.9717	.8299	1.0983	1.9827	784.87
.8000	85.430	85.430	.9718	.9734	.8698	1.0375	2.3516	580.56
.9000	87.759	87.759	.9706	.9765	.9252	1.0064	2.7827	313.16
1.0000	89.726	89.726	.9697	.9816	1.0000	1.0000	3.1027	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 70.160 VL(2) = 113.961

VIRIAL COEFFICIENTS, CC/MOL: B(1,1) = -560.4 B(1,2) = -563.8 B(2,2) = -1260.6

X1	TOTAL PRESSURE, KPA EXPTL.	CALC.	MIXTURE FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	EXCESS GIBBS FUNCTION, J/MOLE
.0000	85.509	85.509	1.0041	.9675	.0000	3.9133	1.0000	0.00
.1000	214.384	214.379	.9703	.9360	.6220	2.8189	1.0143	385.82
.2000	295.332	295.328	.9542	.9219	.7419	2.2737	1.0543	684.65
.3000	341.575	341.574	.9454	.9147	.7887	1.8448	1.1302	892.85
.4000	374.801	374.801	.9392	.9101	.8185	1.5641	1.2348	1012.58
.5000	401.152	401.152	.9342	.9069	.8418	1.3693	1.3767	1050.71
.6000	423.788	423.787	.9299	.9048	.8629	1.2294	1.5704	1009.19
.7000	445.088	445.088	.9258	.9036	.8852	1.1299	1.8374	888.31
.8000	465.567	465.567	.9219	.9036	.9111	1.0594	2.2315	685.10
.9000	485.463	485.463	.9180	.9059	.9454	1.0142	2.8634	390.78
1.0000	505.016	505.016	.9144	.9133	1.0000	1.0000	3.6278	0.00

closely—the cubic splined fits of those data points. Interpolated values (at 0.025 increments in x_1) from the splined fits are fed to the plotting software which then makes its own fit of the input values. Those fits are often not very good if the curve is irregularly shaped. Nevertheless, the curves do help illustrate the scatter and the general behavior of the experimental points. For an accurate determination of how closely the splined fits represent the experimental points, Tables II–V must be used.

The nitromethane and ethanol systems show positive deviations from Raoult's law at all three temperatures. The nitromethane forms an azeotrope at all three temperatures. No azeotropes are formed with ethanol.

The benzene and 1-chlorobutane systems change their mind as the temperature increases (mixed deviation systems). Both systems are almost ideal with small positive deviations at room temperature. At 348 K, the benzene system is still almost ideal but the deviation at high x_1 values has become negative despite the fact that the positive deviation at low x_1 values has increased. The positive deviation in the 1-chlorobutane system increased across the composition range at 348 K but the slight sag at the higher x_1 values is a portent of the behavior at 398 K. At the highest temperature, the positive deviation of the 1-chlorobutane system at low x_1 values has increased further but the deviation is definitely negative at the high x_1 values. The benzene system has become a negative deviation system at all compositions, and the system has become more nonideal. Neither the benzene nor the 1-chlorobutane system forms 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 (*3*). The Peng–Robinson equation of state (*4*) was used for the nitromethane and 1-chlorobutane systems to estimate the vapor-phase fugacity coefficients. The virial equation truncated after the second term was used for the ethanol and benzene systems. The Hayden–O'Connell (*5*) correlation was used to estimate the B_{ii} and B_{ij} values. The equation of state parameters are listed in Tables X and XI.

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 method and show how well that method can reproduce the original pressure data.

The calculated activity coefficient curves are shown in Figure

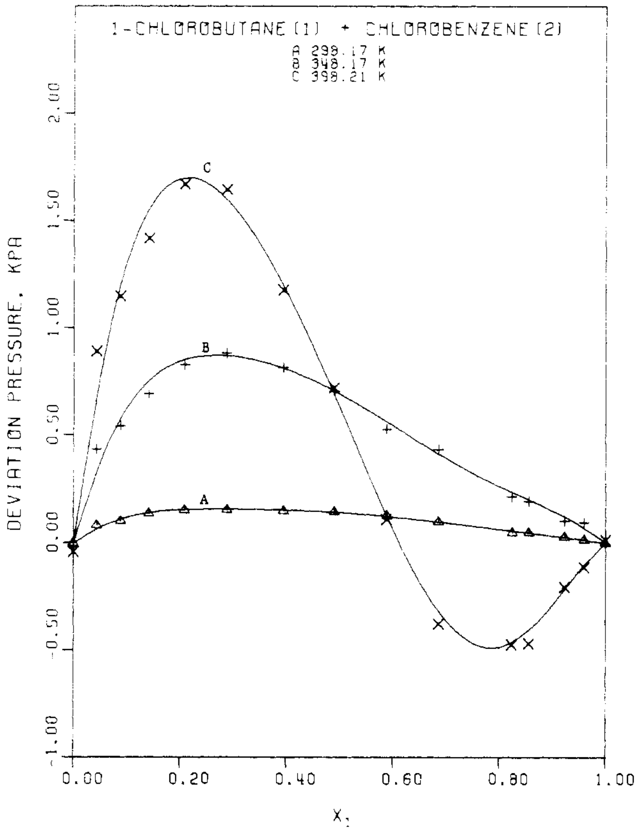

Figure 4. Deviation from Raoult's law for the 1-chlorobutane (1) + chlorobenzene (2) system.

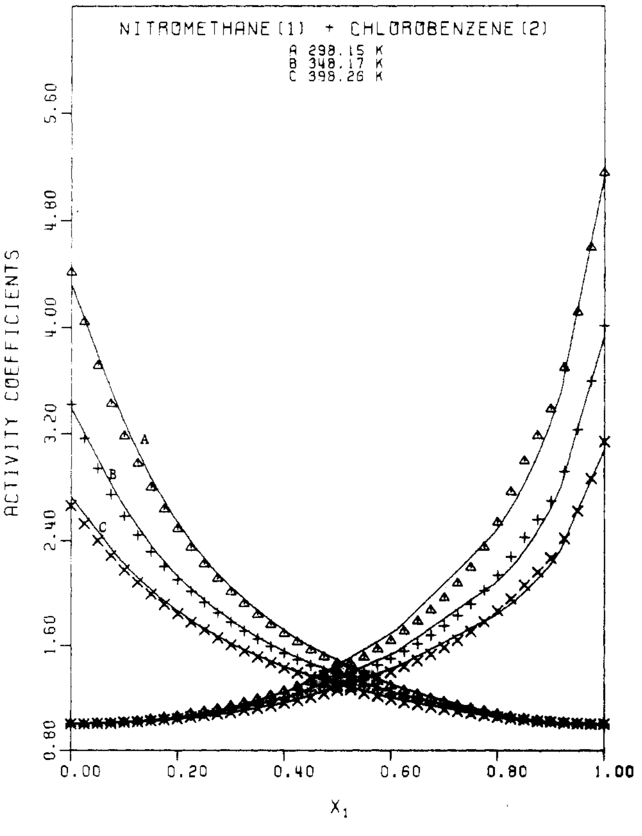

Figure 5. Activity coefficients for the nitromethane (1) + chlorobenzene (2) system. Curves are from Barker results; points are from Mixon et al. method.

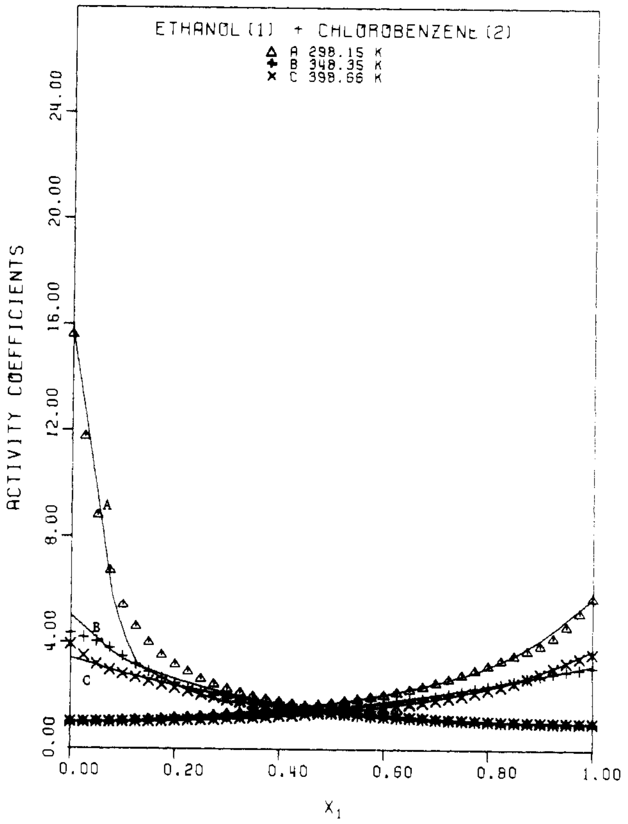

Figure 6. Activity coefficients for the ethanol (1) + chlorobenzene (2) system. Curves are from the Barker results; points are from Mixon et al. method.

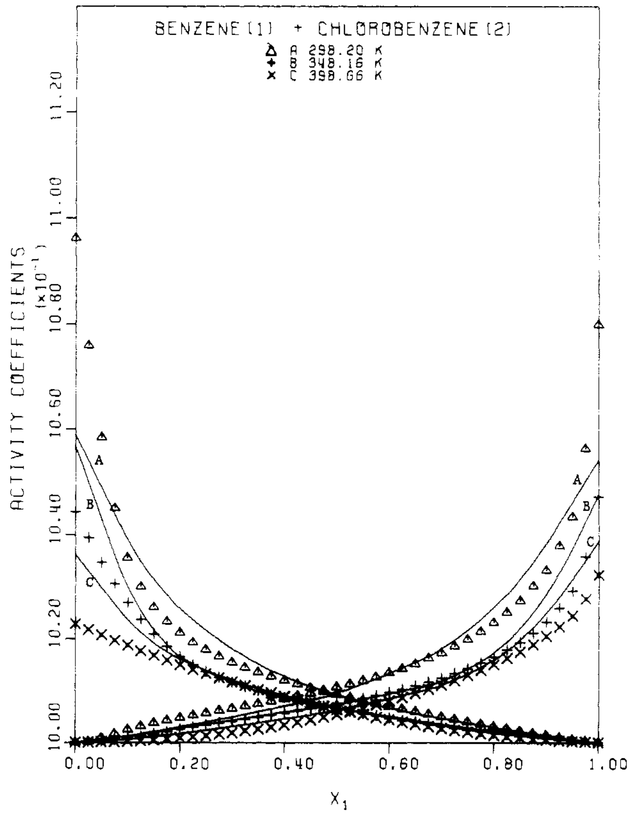

Figure 7. Activity coefficients for the benzene (1) + chlorobenzene (2) system. Curves are from Barker results; points are from Mixon et al. method. Move decimal point one place to left in ordinate scale values.

Table VIII. Calculated Data for the Benzene (1) + Chlorobenzene (2) System at 298.20, 348.16, and 398.66 K Obtained with the Mixon et al. Method and the Virial Equation through B_{ij}

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 89.409 VL(2) = 102.280

VIRIAL COEFFICIENTS, CC/MOL: B(1,1) = -1509.1 B(1,2) = -2068.1 B(2,2) = -3125.7

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	1.635	1.635	.9993	.9979	.0000	1.0962	1.0000	0.00
.1000	2.789	2.789	.9985	.9966	.4705	1.0357	1.0025	14.28
.2000	3.907	3.907	.9977	.9954	.6628	1.0211	1.0048	19.87
.3000	5.023	5.023	.9970	.9943	.7698	1.0155	1.0066	22.87
.4000	6.136	6.136	.9963	.9931	.8380	1.0120	1.0085	24.37
.5000	7.246	7.246	.9956	.9920	.8853	1.0093	1.0107	24.63
.6000	8.353	8.353	.9949	.9909	.9201	1.0070	1.0135	23.68
.7000	9.458	9.458	.9942	.9898	.9468	1.0050	1.0173	21.39
.8000	10.560	10.560	.9936	.9887	.9680	1.0031	1.0231	17.48
.9000	11.660	11.660	.9929	.9876	.9854	1.0014	1.0333	11.27
1.0000	12.757	12.757	.9922	.9865	1.0000	1.0000	1.0799	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 95.342 VL(2) = 107.690

VIRIAL COEFFICIENTS, CC/MOL: B(1,1) = -988.1 B(1,2) = -1300.0 B(2,2) = -1860.2

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	16.338	16.338	.9958	.9895	.0000	1.0443	1.0000	0.00
.1000	23.458	23.457	.9928	.9852	.3697	1.0269	1.0008	9.88
.2000	30.442	30.441	.9901	.9813	.5657	1.0165	1.0026	15.43
.3000	37.413	37.412	.9875	.9775	.6890	1.0117	1.0041	18.42
.4000	44.395	44.394	.9850	.9738	.7741	1.0087	1.0057	19.90
.5000	51.388	51.387	.9826	.9701	.8364	1.0065	1.0075	20.19
.6000	58.394	58.393	.9801	.9665	.8841	1.0047	1.0097	19.35
.7000	65.414	65.413	.9777	.9628	.9219	1.0032	1.0125	17.32
.8000	72.449	72.449	.9753	.9592	.9526	1.0019	1.0165	13.92
.9000	79.502	79.502	.9729	.9556	.9782	1.0008	1.0232	8.72
1.0000	86.574	86.574	.9704	.9519	1.0000	1.0000	1.0472	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 102.570 VL(2) = 113.961

VIRIAL COEFFICIENTS, CC/MOL: B(1,1) = -710.7 B(1,2) = -912.1 B(2,2) = -1260.6

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	85.482	85.482	.9856	.9675	.0000	1.0228	1.0000	0.00
.1000	110.435	110.431	.9789	.9584	.2960	1.0187	1.0002	6.76
.2000	135.441	135.436	.9726	.9499	.4344	1.0150	1.0009	12.11
.3000	160.535	160.528	.9667	.9417	.6153	1.0117	1.0019	16.05
.4000	185.748	185.742	.9609	.9337	.7119	1.0089	1.0034	18.56
.5000	211.115	211.110	.9552	.9257	.7863	1.0064	1.0054	19.62
.6000	236.668	236.664	.9495	.9177	.8457	1.0044	1.0080	19.19
.7000	262.440	262.438	.9438	.9098	.8943	1.0027	1.0111	17.22
.8000	288.465	288.464	.9381	.9018	.9350	1.0014	1.0151	13.60
.9000	314.776	314.776	.9324	.8939	.9698	1.0005	1.0205	8.12
1.0000	341.406	341.406	.9266	.8858	1.0000	1.0000	1.0323	0.00

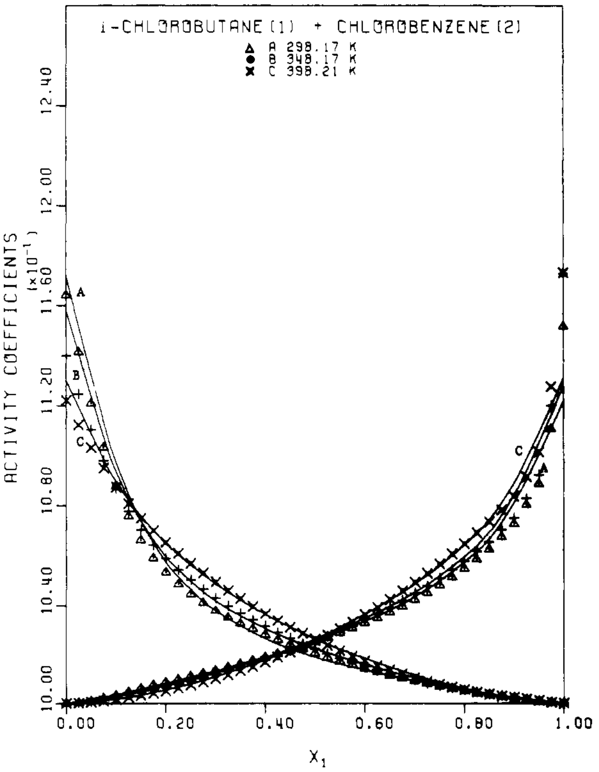

Figure 8. Activity coefficients for the 1-chlorobutane (1) + chlorobenzene (2) system. Curves are from Barker results; points are from Mixon et al. method. Move decimal point one place to left in ordinate scale values.

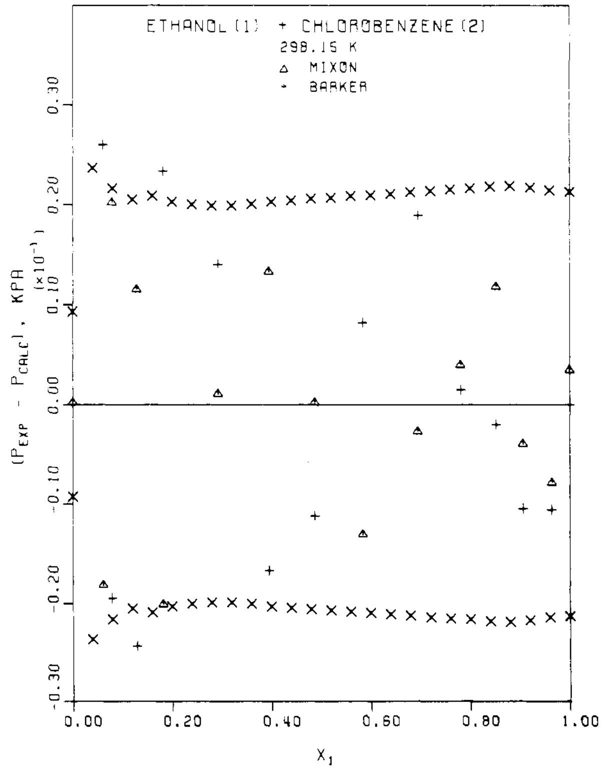

Figure 9. Comparison of the Barker and Mixon et al. results on the resolution error plot for ethanol (1) + chlorobenzene (2) at 348.35 K. Move decimal pont one place to left in ordinate scale values.

Table IX. Calculated Data for the 1-Chlorobutane (1) + Chlorobenzene (2) System at 298.17, 348.17, and 398.21 K Obtained with the Mixon et al. Method and the Peng-Robinson Equation of State

```
LIQUID MOLAR VOLUMES, CC/MOL: VL(1) =  105.126   VL(2) =  102.282

                                                                                        EXCESS
                                       MIXTURE FUGACITY                                 GIBBS
           TOTAL PRESSURE, KPA           COEFFICIENTS                ACTIVITY COEFFICIENTS   FUNCTION,
  X1        EXPTL.       CALC.           1        2          Y1           1          2         J/MOLE
 .0000       1.641       1.641         .9991    .9989       .0000       1.1641     1.0000        0.00
 .1000       2.959       2.959         .9984    .9981       .4989       1.0879     1.0033       28.26
 .2000       4.187       4.187         .9978    .9973       .6832       1.0532     1.0087       42.89
 .3000       5.398       5.398         .9971    .9965       .7838       1.0379     1.0135       51.02
 .4000       6.598       6.598         .9965    .9957       .8475       1.0279     1.0188       55.02
 .5000       7.787       7.787         .9959    .9949       .9916       1.0203     1.0250       55.55
 .6000       8.967       8.967         .9952    .9942       .9240       1.0141     1.0327       52.74
 .7000      10.141      10.141         .9946    .9934       .9491       1.0091     1.0422       46.51
 .8000      11.313      11.313         .9940    .9927       .9692       1.0052     1.0546       36.59
 .9000      12.485      12.485         .9934    .9919       .9858       1.0022     1.0726       22.33
1.0000      13.654      13.654         .9927    .9911      1.0000       1.0000     1.1516        0.00
```

```
LIQUID MOLAR VOLUMES, CC/MOL: VL(1) =  112.244   VL(2) =  107.690

                                                                                        EXCESS
                                       MIXTURE FUGACITY                                 GIBBS
           TOTAL PRESSURE, KPA           COEFFICIENTS                ACTIVITY COEFFICIENTS   FUNCTION,
  X1        EXPTL.       CALC.           1        2          Y1           1          2         J/MOLE
 .0000      16.299      16.299         .9943    .9928       .0000       1.1401     1.0000        0.00
 .1000      24.413      24.413         .9913    .9892       .3954       1.0869     1.0024       30.27
 .2000      32.092      32.091         .9886    .9859       .5878       1.0589     1.0068       48.78
 .3000      39.631      39.630         .9859    .9826       .7054       1.0430     1.0118       60.37
 .4000      47.072      47.071         .9833    .9793       .7854       1.0314     1.0179       66.63
 .5000      54.448      54.447         .9806    .9761       .8437       1.0222     1.0253       68.06
 .6000      61.791      61.790         .9780    .9729       .8885       1.0151     1.0342       64.91
 .7000      69.126      69.126         .9754    .9697       .9242       1.0095     1.0448       57.23
 .8000      76.479      76.479         .9728    .9666       .9536       1.0054     1.0577       44.92
 .9000      83.870      83.870         .9702    .9633       .9784       1.0026     1.0750       27.56
1.0000      91.216      91.216         .9676    .9602      1.0000       1.0000     1.1726        0.00
```

```
LIQUID MOLAR VOLUMES, CC/MOL: VL(1) =  121.277   VL(2) =  113.900

                                                                                        EXCESS
                                       MIXTURE FUGACITY                                 GIBBS
           TOTAL PRESSURE, KPA           COEFFICIENTS                ACTIVITY COEFFICIENTS   FUNCTION,
  X1        EXPTL.       CALC.           1        2          Y1           1          2         J/MOLE
 .0000      84.573      84.573         .9793    .9737       .0000       1.1220     1.0000        0.00
 .1000     112.856     112.853         .9722    .9650       .3177       1.0873     1.0016       32.42
 .2000     140.171     140.167         .9654    .9566       .5052       1.0652     1.0051       55.36
 .3000     167.061     167.058         .9587    .9484       .6314       1.0495     1.0101       71.26
 .4000     193.665     193.662         .9521    .9403       .7231       1.0367     1.0168       80.79
 .5000     220.107     220.105         .9456    .9322       .7933       1.0260     1.0254       84.11
 .6000     246.519     246.518         .9391    .9242       .8494       1.0173     1.0362       81.16
 .7000     273.053     273.052         .9326    .9162       .8957       1.0105     1.0492       71.89
 .8000     299.863     299.863         .9260    .9081       .9351       1.0056     1.0647       56.22
 .9000     327.089     327.089         .9193    .8999       .9694       1.0025     1.0836       33.97
1.0000     354.376     354.376         .9126    .8917      1.0000       1.0000     1.1731        0.00
```

Table X. Parameters for Peng-Robinson Equation (*4*)[a]

component	T_c, K	P_c, MPa	ω
nitromethane	588.0	6.313	0.3460
1-chlorobutane	542.0	3.688	0.2180
chlorobenzene	632.4	4.520	0.2490

[a] Binary interaction constant was set at 0.0 for all systems.

Table XI. Virial Coefficient Values (*5*)

system	*T*, K	B_{11}	B_{12}	B_{22}
ethanol (1) + chlorobenzene (2)	298.15	−2169	−1186	−3128
	348.35	−977	−786	−1857
	398.66	−560	−564	−1261
benzene (1) + chlorobenzene (2)	298.20	−1509	−2068	−3126
	348.16	−988	−1300	−1860
	398.66	−711	−912	−1261

5-8 for both the Mixon et al. and the Barker (*6*) data reduction methods. The Barker results shown used the five-constant Redlich-Kister equation to represent G^E and used the same equations of state as the Mixon et al. calculation (see Tables X and XI).

Table XII. Comparison of the Barker and Mixon et al. Results

	max % dev in P[a]		rms for % dev[b]	
temp, K	Barker	Mixon	Barker	Mixon
Nitromethane (1) + Chlorobenzene (2), Peng-Robinson				
298.15	0.285	0.190	0.140	0.079
348.17	0.072	0.106	0.040	0.045
398.26	0.059	0.055	0.030	0.024
Ethanol (1) + Chlorobenzene (2), Virial, Hayden-O'Connell				
298.15	0.490	0.360	0.243	0.181
348.35	0.786	0.266	0.297	0.133
398.16	0.544	0.261	0.186	0.109
Benzene (1) + Chlorobenzene (2), Virial, Hayden-O'Connell				
298.20	0.316	0.276	0.123	0.107
348.16	0.099	0.066	0.036	0.033
398.66	0.051	0.122	0.024	0.044
1-Chlorobutane (1) + Chlorobenzene (2), Peng-Robinson				
298.17	0.449	0.428	0.164	0.163
348.17	0.335	0.349	0.106	0.115
398.21	0.158	0.144	0.585	0.049

[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. Effect of Calculation Method on γ_i^∞ Values for the Ethanol (1) + Chlorobenzene (2) System[a]

	accuracy of P fits, max % dev/rmsd			calcd γ_i^∞ values					
				component 1			component 2		
calculation method	298.15 K	348.35 K	398.16 K	298.15 K	348.35 K	398.16 K	298.15 K	348.35 K	398.16 K
Mixon et al.	0.4/0.2	0.3/0.1	0.3/0.1	15.562	4.271	3.822	5.566	2.905	3.154
Barker:									
absolute Van Laar	5.7/2.6	1.3/3.8	0.8/0.4	10.959	5.135	3.565	4.330	3.144	3.302
Wilson	0.9/0.4	2.4/0.9	1.5/0.6	17.270	5.651	3.735	5.375	3.345	3.468
NRTL	1.4/0.7	1.1/0.4	0.9/0.4	14.636	5.092	3.610	5.776	3.118	3.348
modified Margules	0.1/0.0	1.7/0.6	2.0/0.7	20.079	4.825	3.459	5.236	3.017	3.549
UNIQUAC	4.7/2.3	1.2/0.4	0.9/0.4	11.602	5.150	3.588	4.422	3.106	3.316
Redlich-Kister, five constants	0.5/0.2	0,8/0.3	0.5/0.2	15.809	4.916	3.317	5.594	2.930	3.268
Gautreaux-Coates:									
splined fits				15.519	4.228	3.843	5.547	2.903	3.135
P_D/x_1x_2 plots					4.453	3.450	5.323	3.090	3.276

[a] Virial equation, Tsonopoulous correlation (7).

Table XIV. Effect of Equation of State Choice on γ_i^∞ Values Obtained with Mixon et al. Method for Ethanol (1) + Chlorobenzene (2) at 398.16 K

	γ_i^∞	
eq of state used	1	2
ideal gas	3.6839	3.6369
virial through B_{ij}:		
Tsonopolous (7)	3.8218	3.1537
Hayden-O'Connell (5)	3.9133	3.6278
Redlich-Kwong, Lu modification (11)	3.7938	3.3872

The points in Figures 5–8 are the evenly spaced Mixon et al. values while the curves represent the Barker results. (As in the case of the P_D curves in Figures 1–4, the curves plotted are approximations by the plotting software of the Barker input values; hence, small irregularities in the shapes of the curves are usually the fault of the plotting program rather than the Barker fit.) Both methods agreed very well for the nitromethane data sets but not so well for the other systems.

As shown in Table XII, the two methods reproduced the experimental P values at about the same level of accuracy for all systems but the ethanol system. A further comparison for that system is shown in Table XIII. Of the six G^E correlations tried with the Barker method, only the five-constant Redlich-Kister equation reproduced the experimental P values at a level close to that of the Mixon et al. results. (The maximum percent deviation and root-mean-squared deviation (rmsd) values tabulated were calculated as shown at the bottom of Table XII.) However, as shown in the resolution error band plot in Figure 9, some of the Barker points fell outside the error band even with the Redlich-Kister equation. The zero line in Figure 9 represents the experimental P values. The boundaries formed by the large X's represent the maximum plus or minus experimental errors which could result due to the resolution limitations of the devices used to measure the pressure, temperature, and mole fraction values. The formula used to calculate the maximum possible resolution errors has been given in a previous paper (8). The resolution error does not include errors such as operator error, inadequate degassing, chemical reactions, etc. (Note that the 10^{-1} multiplier on the ordinate scale in Figure 9 means that the decimal point is to be moved one place to the left in the ordinate scale values.)

As shown in the Table XIII, the ethanol + chlorobenzene system is a difficult one for the popular G^E correlations. Note the variation in the γ_i^∞ values, particularly at 298.15 K. The Redlich-Kister equation gives γ_i^∞ values which agree fairly well with the Mixon et al. results but even that equation has trouble with the 298.15 K data set as shown in Figures 6 and 9.

The use of the P_D/x_1x_2 plots along with the Gautreaux-Coates equations (9) to obtain γ_i^∞ values has been discussed previously (10). The $(dP/dx_1)_i^\infty$ values needed by the Gautreaux-Coates equation were obtained both from the cubic splined fits and from extrapolation of the P_D/x_1x_2 plots. The P_D/x_1x_2 plot could not be extrapolated with any certainty at 298.15 K for the ethanol + chlorobenzene system but otherwise the Gautreaux-Coates results support the general validity of the γ_i^∞ values from the Mixon et al. method for that system.

The Mixon et al. "curves" in Figure 7 for the benzene + chlorobenzene system are very nicely spaced and are probably more reliable than the Barker results.

The activity coefficients for the 1-chlorobutane + chlorobenzene system do not vary much with temperature (see Figure 8). When the curves lie so close together, it is difficult to avoid crossing even when such crossing should not occur. From the shapes of the P_D curves for this system (see Figure 4), crossing of the activity coefficient curves was not unexpected. The Barker and Mixon et al. results agreed reasonably well except for the intercepts at $x_1 = 1.0$.

Besides depending upon the data reduction method used, the calculated y_i, γ_i, and G^E values depend upon the equation of state used for the vapor-phase fugacity coefficients. An indication of the magnitude of the effect on the γ_i values is given in Table XIV. The pressure for the ethanol + chlorobenzene system at 298.16 K ranged from 85.5 to 504.7 kPa.

Registry No. Chlorobenzene, 108-90-7; nitromethane, 75-52-5; ethanol, 64-17-5; 1-chlorobutane, 109-69-3; benzene, 71-43-2.

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