J. Chem. Eng. Data **1983**, *28*, 412–419

same surface, and Figure 3 is a contour diagram showing lines of constant P.

The only azeotrope is for the water/ethanol binary system at x_1 = 0.0641 and P^{az} = 29.537 kPa.

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

Greek Letters

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

Registry No. Ethylene glycol, 107-21-1; ethanol, 64-17-5.

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Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of Dichloromethane with Pentane, Acetone, Ethyl Acetate, Methanol, and Acetonitrile

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Total-pressure vapor–liquid equilibrium (VLE) data are reported at approximately 298, 348, and 398 K for dichloromethane with pentane, acetone, ethyl acetate, methanol, and acetonitrile. 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 and the results compared. Six G^E correlations were tested in the Barker data reduction; the five-constant Redlich–Kister equation gave the best results. The Peng–Robinson equation of state was used for all the data reduction calculations.

Introduction

This paper presents total-pressure vapor–liquid equilibrium (VLE) data for five binary systems for dichloromethane with pentane, acetone, ethyl acetate, methanol, and acetonitrile. Data for each binary were measured at approximately 298, 348, and 398 K. The techniques and apparatus used to measure these data have been described previously along with the defining equation for the activity coefficient and the standard states used (*1*).

Chemicals Used

The sources and the purities of the chemicals used are given 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, each chemical was poured into a distillation flask and distilled through a Vigreux column (25-mm o.d. and 470 mm long). The first and last portions of each distillate were discarded. The retained portions were caught in amber bottles and back-flushed with dry nitrogen for transfer to the cell-loading operation. The stated purities of the chemicals were confirmed by gas–liquid chromatography.

None of the compounds exhibited any degradation during the VLE measurements. The cell pressures were stable with re-

Table I. Chemicals Used

component	vendor	stated purity, %
ethyl acetate	Burdick and Jackson	99.9
acetone	Burdick and Jackson	99.9+
methanol	Fisher Scientific	99.9
pentane	Burdick and Jackson	99.9
acetonitrile	Burdick and Jackson	99.9+
dichloromethane	Burdick and Jackson	99.9

Table II. Experimental P vs. x_1 Data for the Pentane (1) + Dichloromethane (2) System

298.19 K			348.17 K			398.16 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	58.35	58.36	0.0	308.1	308.1	0.0	1030.1	1030.2
0.0331	63.98	63.95	0.0329	325.8	325.8	0.0329	1061.4	1061.4
0.0857	69.49	69.56	0.0854	343.2	343.3	0.0853	1097.1	1097.4
0.1510	74.24	74.18	0.1506	358.5	358.3	0.1504	1131.6	1130.9
0.2213	77.46	77.49	0.2209	369.6	369.7	0.2207	1157.1	1157.3
0.3012	79.84	79.84	0.3009	377.9	378.1	0.3007	1176.0	1176.6
0.4097	81.74	81.74	0.4095	384.2	384.1	0.4097	1187.6	1187.1
0.5011	82.46	82.45	0.5012	385.4	385.2	0.5016	1184.2	1183.7
0.5970	82.39	82.42	0.5975	382.6	382.9	0.5987	1169.3	1169.8
0.6945	81.61	81.58	0.6948	377.3	377.2	0.6954	1147.1	1147.3
0.7792	79.90	79.90	0.7796	368.8	368.8	0.7801	1121.4	1120.9
0.8185	78.73	78.73	0.8189	363.4	363.5	0.8194	1105.9	1105.9
0.8998	75.30	75.33	0.9002	349.5	349.4	0.9005	1066.8	1067.1
0.9497	72.45	72.43	0.9500	338.0	338.1	0.9502	1037.5	1037.3
1.0000	68.41	68.41	1.0000	323.9	323.9	1.0000	1003.3	1003.3

0021-9568/83/1728-0412$01.50/0

Table III. Experimental P vs. x_1 Data for the Dichloromethane (1) + Acetone (2) System

298.19 K			348.16 K			398.15 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	30.86	30.86	0.0	186.33	186.35	0.0	679.8	679.8
0.0506	31.05	31.04	0.0506	187.81	187.78	0.0506	684.6	684.6
0.0868	31.20	31.20	0.0868	188.88	188.86	0.0867	688.4	688.4
0.1543	31.54	31.57	0.1543	191.16	191.21	0.1542	696.6	696.8
0.2193	32.11	32.09	0.2192	194.14	194.16	0.2190	707.0	706.9
0.3183	33.33	33.32	0.3180	200.56	200.54	0.3172	727.1	726.9
0.3971	34.77	34.78	0.3969	207.59	207.49	0.3965	747.4	747.4
0.4919	37.18	37.19	0.4916	218.03	218.17	0.4912	777.1	777.2
0.5912	40.42	40.43	0.5908	231.96	231.94	0.5903	814.8	814.9
0.6924	44.40	44.38	0.6921	248.60	248.53	0.6916	860.0	859.9
0.7857	48.46	48.48	0.7854	265.79	265.83	0.7850	906.9	906.9
0.8378	50.88	50.87	0.8375	276.1	276.1	0.8372	935.1	935.1
0.9167	54.54	54.53	0.9165	292.3	292.2	0.9163	979.6	979.6
0.9599	56.49	56.50	0.9599	301.0	301.1	0.9597	1004.8	1004.8
1.0000	58.22	58.22	1.0000	308.7	308.7	1.0000	1028.1	1028.1

Table IV. Experimental P vs. x_1 Data for the Dichloromethane (1) + Ethyl Acetate (2) System

298.21 K			348.15 K			398.17 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	12.674	12.674	0.0	94.73	94.73	0.0	393.5	393.5
0.0486	13.581	13.580	0.0485	99.23	99.24	0.0484	408.7	408.7
0.0987	14.495	14.497	0.0986	104.13	104.10	0.0983	424.2	424.2
0.1539	15.705	15.708	0.1536	110.36	110.37	0.1532	443.6	443.6
0.1970	16.820	16.809	0.1967	115.87	115.90	0.1961	460.5	460.6
0.3032	20.046	20.057	0.3029	131.61	131.58	0.3023	507.7	507.6
0.3956	23.614	23.608	0.3951	148.05	148.00	0.3942	555.2	555.3
0.4945	28.26	28.27	0.4939	168.94	169.04	0.4930	615.2	615.1
0.5895	33.47	33.45	0.5890	192.42	192.36	0.5880	680.6	680.7
0.6884	39.36	39.39	0.6879	219.25	219.23	0.6869	756.7	756.6
0.7801	45.20	45.19	0.7796	245.66	245.69	0.7789	832.7	833.0
0.8339	48.66	48.64	0.8336	261.55	261.55	0.8328	880.3	880.0
0.9160	53.66	53.68	0.9158	285.6	285.6	0.9154	953.9	954.0
0.9594	56.14	56.13	0.9593	297.8	297.8	0.9590	992.8	992.8
1.0000	58.28	58.28	1.0000	308.5	308.5	1.0000	1028.4	1028.4

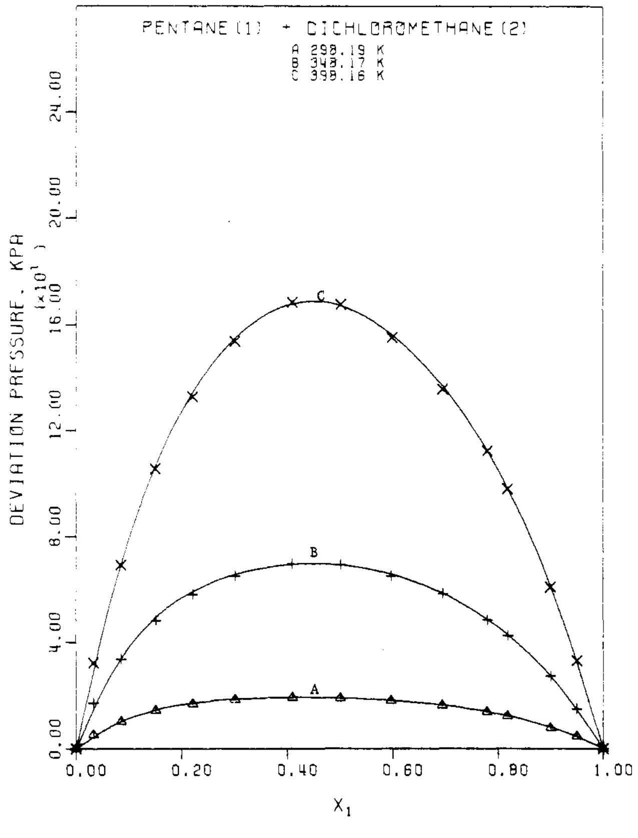

Figure 1. Deviation from Raoult's law for the pentane (1) + dichloromethane (2) system. The ×10^1 multiplier means that the decimal point in the ordinate scale values must be moved one place to the right.

spect to time, and all liquids were perfectly clear when removed from the cells at the end of the last isotherm.

Table V. Experimental P vs. x_1 Data for the Dichloromethane (1) + Methanol (2) System

298.18 K			348.15 K			398.21 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	16.999	16.996	0.0	151.26	151.27	0.0	737.2	737.1
0.0429	23.214	23.235	0.0427	181.44	181.41	0.0425	826.3	826.8
0.0868	29.12	29.08	0.0865	208.61	208.61	0.0861	902.9	902.5
0.1439	35.92	35.96	0.1435	238.79	238.87	0.1429	984.0	983.4
0.2149	43.27	43.25	0.2144	269.27	269.19	0.2139	1060.8	1061.7
0.3773	54.16	54.20	0.3767	314.0	314.0	0.3762	1168.7	1168.4
0.4066	55.55	55.47	0.4063	319.3	319.3	0.4063	1180.5	1180.4
0.4722	57.66	57.71	0.4717	328.5	328.6	0.4715	1200.3	1200.6
0.5658	59.83	59.84	0.5655	337.7	337.6	0.5656	1219.0	1218.2
0.6616	61.26	61.22	0.6614	343.4	343.4	0.6618	1223.0	1224.1
0.7593	62.01	62.06	0.7593	345.9	345.9	0.7601	1212.4	1212.0
0.8082	62.34	62.32	0.8084	345.6	345.6	0.8139	1194.9	1194.7
0.8964	62.49	62.49	0.8966	340.0	340.0	0.8971	1147.0	1147.0
0.9470	61.91	61.92	0.9472	330.9	330.9	0.9476	1099.4	1099.6
1.0000	58.19	58.19	1.0000	308.3	308.3	1.0000	1030.2	1030.1

Table VI. Experimental P vs. x_1 Data for the Dichloromethane (1) + Acetonitrile (2) System

298.23 K			348.15 K			398.13 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	11.880	11.881	0.0	82.10	82.11	0.0	336.6	336.6
0.0440	14.357	14.354	0.0439	94.80	94.75	0.0437	375.4	375.4
0.0901	16.823	16.827	0.0899	107.25	107.26	0.0897	413.8	413.7
0.1498	19.865	19.864	0.1495	122.53	122.56	0.1490	460.6	460.6
0.2090	22.716	22.718	0.2086	137.07	137.11	0.2080	505.4	505.5
0.2967	26.781	26.776	0.2962	157.83	157.73	0.2955	569.8	569.6
0.3900	31.03	31.04	0.3895	178.79	178.79	0.3887	634.3	634.6
0.4923	35.65	35.66	0.4918	201.06	201.15	0.4909	702.6	702.4
0.5911	40.06	40.05	0.5906	222.26	222.20	0.5898	765.9	766.0
0.6664	43.38	43.38	0.6660	238.01	237.99	0.6653	814.0	814.0
0.7741	48.12	48.13	0.7737	260.33	260.35	0.7731	882.3	882.1
0.8327	50.73	50.73	0.8324	272.58	272.57	0.8319	918.9	919.0
0.9191	54.61	54.60	0.9189	290.7	290.7	0.9186	973.3	973.3
0.9593	56.43	56.43	0.9592	299.3	299.3	0.9591	998.8	998.8
1.0000	58.25	58.25	1.0000	308.0	308.0	1.0000	1024.9	1024.9

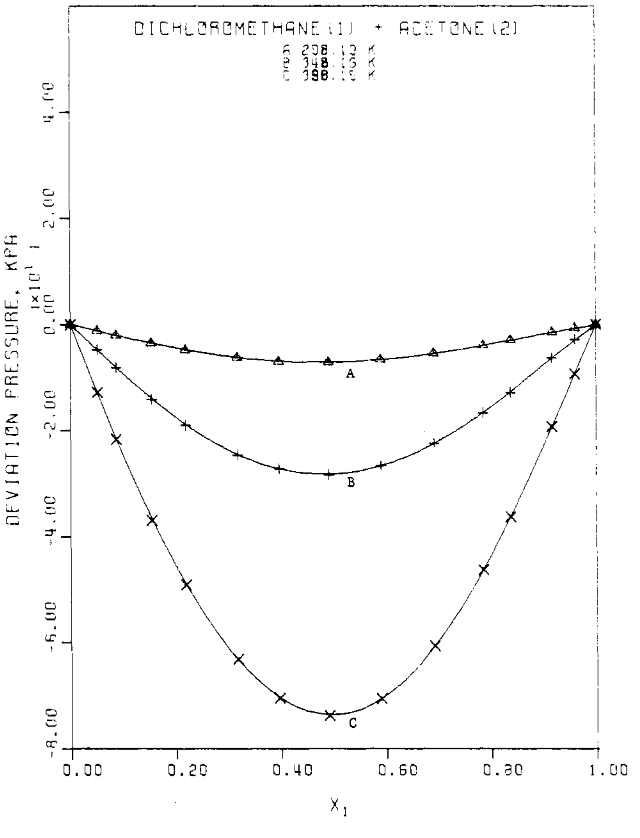

Figure 2. Deviation from Raoult's law for the system dichloromethane (1) + acetone (2). The ×10^1 notation is explained in Figure 1.

Experimental Data

Tables II–VI present the experimental *PTx* data. The "smooth" pressure values reported are from the least-squares

Table VII. Calculated Data for the Pentane (1) + Dichloromethane (2) System at 298.19 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 116.19 COMPONENT 2 = 64.49

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	58.358	58.358	0.9771	0.9841	0.0	3.7830	1.0000	0.0
0.050	66.079	66.077	0.9737	0.9820	0.1539	2.9788	1.0061	149.59
0.100	70.722	70.720	0.9717	0.9808	0.2389	2.4688	1.0210	270.46
0.150	74.123	74.122	0.9703	0.9799	0.3008	2.1682	1.0399	370.30
0.200	76.636	76.636	0.9692	0.9793	0.3481	1.9435	1.0643	453.04
0.250	78.464	78.464	0.9684	0.9788	0.3855	1.7611	1.0951	519.74
0.300	79.809	79.809	0.9678	0.9785	0.4169	1.6132	1.1321	571.01
0.350	80.845	80.846	0.9674	0.9782	0.4458	1.4971	1.1735	607.91
0.400	81.621	81.621	0.9670	0.9780	0.4730	1.4027	1.2202	631.59
0.450	82.151	82.151	0.9668	0.9779	0.4987	1.3227	1.2743	642.54
0.500	82.449	82.450	0.9666	0.9779	0.5230	1.2528	1.3385	640.79
0.550	82.530	82.531	0.9665	0.9779	0.5485	1.1954	1.4092	626.15
0.600	82.410	82.410	0.9666	0.9780	0.5792	1.1555	1.4755	600.81
0.650	82.086	82.087	0.9667	0.9781	0.6091	1.1174	1.5605	565.10
0.700	81.505	81.506	0.9669	0.9783	0.6409	1.0844	1.6609	517.95
0.750	80.603	80.604	0.9672	0.9786	0.6772	1.0579	1.7727	459.48
0.800	79.314	79.316	0.9677	0.9790	0.7195	1.0375	1.8957	390.07
0.850	77.576	77.577	0.9684	0.9796	0.7695	1.0222	2.0327	310.10
0.900	75.322	75.323	0.9692	0.9803	0.8291	1.0110	2.1969	219.55
0.950	72.414	72.414	0.9704	0.9812	0.9019	1.0030	2.4278	116.98
1.000	68.412	68.412	0.9720	0.9825	1.0000	1.0000	2.7314	0.0

Table VIII. Calculated Data for the Pentane (1) + Dichloromethane (2) System at 348.17 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 127.12 COMPONENT 2 = 69.32

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	308.143	308.143	0.9210	0.9441	0.0	2.8372	1.0000	0.0
0.050	332.517	332.508	0.9141	0.9397	0.1099	2.2568	1.0058	133.68
0.100	347.089	347.083	0.9099	0.9372	0.1791	1.9100	1.0189	236.03
0.150	358.181	358.178	0.9067	0.9353	0.2362	1.7257	1.0335	318.04
0.200	366.750	366.749	0.9042	0.9338	0.2846	1.5918	1.0513	385.01
0.250	373.217	373.219	0.9023	0.9328	0.3263	1.4824	1.0732	438.33
0.300	378.007	378.009	0.9009	0.9320	0.3636	1.3914	1.0993	478.66
0.350	381.485	381.487	0.8998	0.9315	0.3984	1.3171	1.1287	506.80
0.400	383.789	383.792	0.8991	0.9312	0.4313	1.2540	1.1624	523.44
0.450	384.993	384.995	0.8986	0.9311	0.4627	1.1990	1.2015	528.77
0.500	385.174	385.177	0.8984	0.9312	0.4951	1.1549	1.2428	523.04
0.550	384.406	384.407	0.8985	0.9315	0.5312	1.1242	1.2801	508.15
0.600	382.765	382.765	0.8988	0.9320	0.5690	1.0997	1.3190	485.61
0.650	380.278	380.277	0.8993	0.9326	0.6071	1.0767	1.3663	455.31
0.700	376.800	376.799	0.9001	0.9335	0.6465	1.0561	1.4222	416.56
0.750	372.152	372.151	0.9012	0.9345	0.6889	1.0389	1.4853	369.14
0.800	366.156	366.155	0.9026	0.9359	0.7356	1.0251	1.5550	313.10
0.850	358.631	358.631	0.9045	0.9375	0.7880	1.0147	1.6318	248.57
0.900	349.398	349.398	0.9069	0.9395	0.8474	1.0071	1.7200	175.54
0.950	338.131	338.130	0.9098	0.9419	0.9161	1.0019	1.8354	93.21
1.000	323.905	323.905	0.9135	0.9449	1.0000	1.0000	1.9810	0.0

Table IX. Calculated Data for the Pentane (1) + Dichloromethane (2) System at 398.16 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 143.44 COMPONENT 2 = 75.79

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	1030.157	1030.157	0.8224	0.8711	0.0	1.9300	1.0000	0.0
0.050	1074.599	1074.599	0.8137	0.8657	0.0795	1.6871	1.0034	97.11
0.100	1105.773	1105.774	0.8075	0.8619	0.1421	1.5371	1.0106	173.78
0.150	1130.746	1130.751	0.8025	0.8590	0.1977	1.4471	1.0193	237.25
0.200	1150.558	1150.564	0.7984	0.8568	0.2473	1.3733	1.0307	289.97
0.250	1165.653	1165.662	0.7952	0.8551	0.2920	1.3079	1.0453	332.27
0.300	1176.476	1176.485	0.7928	0.8541	0.3328	1.2496	1.0636	364.15
0.350	1183.438	1183.454	0.7912	0.8535	0.3710	1.1979	1.0854	385.64
0.400	1186.825	1186.840	0.7901	0.8534	0.4073	1.1525	1.1109	396.81
0.450	1186.885	1186.905	0.7897	0.8537	0.4438	1.1156	1.1378	398.03
0.500	1183.868	1183.890	0.7898	0.8544	0.4823	1.0887	1.1631	390.73
0.550	1178.023	1178.047	0.7905	0.8556	0.5230	1.0692	1.1865	376.49
0.600	1169.602	1169.626	0.7916	0.8571	0.5660	1.0548	1.2083	356.53
0.650	1158.852	1158.880	0.7931	0.8589	0.6109	1.0438	1.2295	331.69
0.700	1146.024	1146.050	0.7950	0.8611	0.6574	1.0345	1.2527	302.37
0.750	1131.147	1131.177	0.7974	0.8635	0.7046	1.0251	1.2833	268.08
0.800	1113.588	1113.615	0.8002	0.8664	0.7535	1.0163	1.3223	227.80
0.850	1092.585	1092.605	0.8038	0.8696	0.8058	1.0089	1.3687	180.82
0.900	1067.377	1067.395	0.8081	0.8735	0.8632	1.0036	1.4203	126.81
0.950	1037.447	1037.458	0.8133	0.8781	0.9276	1.0008	1.4691	66.13
1.000	1003.281	1003.281	0.8193	0.8833	1.0000	1.0000	1.5133	0.0

cubic splined fits used to provide the evenly spaced values required by the finite-difference Mixon–Gumowski–Carpenter method (*2*) for the reduction of *PTx* data.

Figures 1–5 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.

Table X. Calculated Data for the Dichloromethane (1) + Acetone (2) System at 298.19 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 64.49 COMPONENT 2 = 74.04

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EKPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	30.864	30.864	0.9918	0.9885	0.0	0.5915	1.0000	0.0
0.050	31.042	31.042	0.9918	0.9884	0.0557	0.5994	0.9996	-64.34
0.100	31.259	31.258	0.9917	0.9884	0.1132	0.6130	0.9977	-126.41
0.150	31.541	31.540	0.9916	0.9883	0.1736	0.6321	0.9933	-184.77
0.200	31.917	31.916	0.9914	0.9881	0.2371	0.6553	0.9857	-238.19
0.250	32.411	32.411	0.9913	0.9880	0.3035	0.6813	0.9746	-285.77
0.300	33.047	33.047	0.9911	0.9877	0.3721	0.7095	0.9597	-326.77
0.350	33.849	33.848	0.9909	0.9875	0.4418	0.7394	0.9407	-360.50
0.400	34.839	34.838	0.9906	0.9871	0.5116	0.7708	0.9175	-386.31
0.450	36.034	36.034	0.9902	0.9867	0.5798	0.8029	0.8902	-403.55
0.500	37.426	37.426	0.9898	0.9862	0.6443	0.8337	0.8604	-411.91
0.550	39.002	39.002	0.9894	0.9856	0.7040	0.8625	0.8287	-411.38
0.600	40.748	40.748	0.9889	0.9850	0.7581	0.8890	0.7954	-402.01
0.650	42.651	42.651	0.9884	0.9844	0.8065	0.9133	0.7604	-383.76
0.700	44.699	44.699	0.9878	0.9836	0.8493	0.9353	0.7237	-356.54
0.750	46.870	46.870	0.9872	0.9829	0.8865	0.9549	0.6853	-320.11
0.800	49.130	49.130	0.9866	0.9821	0.9182	0.9713	0.6462	-274.31
0.850	51.440	51.440	0.9860	0.9812	0.9449	0.9843	0.6070	-219.10
0.900	53.761	53.761	0.9853	0.9804	0.9671	0.9936	0.5680	-154.52
0.950	56.050	56.050	0.9847	0.9796	0.9853	0.9991	0.5304	-80.64
1.000	58.218	58.218	0.9841	0.9788	1.0000	1.0000	0.5259	0.0

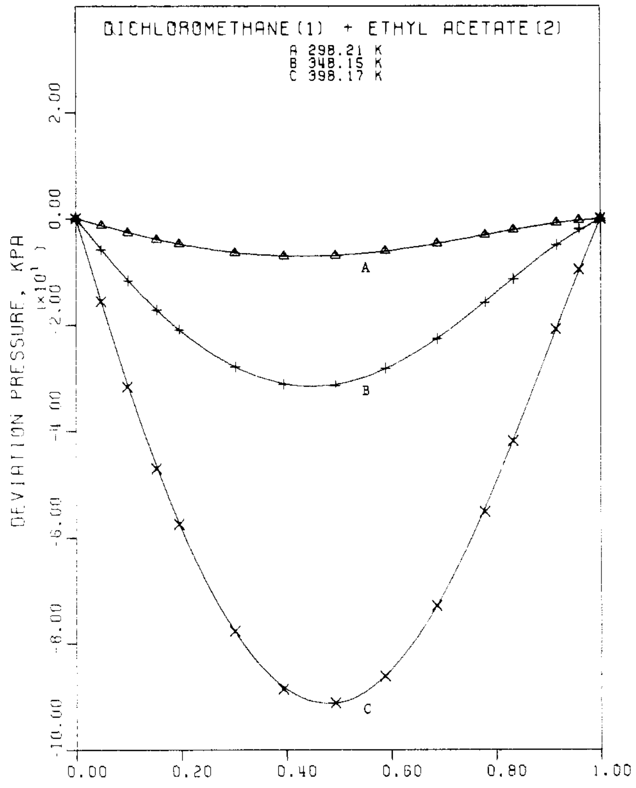

Figure 3. Deviation from Raoult's law for the system dichloromethane (1) + ethyl acetate (2). The $\times 10^1$ notation is explained in Figure 1.

The point symbols in Figures 1–5 denote the experimental data points and they are positioned exactly. The curves are drawn by the plotting software and are not an exact representation of the splined fits. For an actual comparison of the splined-fit values and the experimental P values, see Tables II–VI.

Dichloromethane shows positive deviations from Raoult's law at all temperatures with pentane, methanol, and acetonitrile. It shows negative deviations at all temperatures with acetone and ethyl acetate. Azeotropes are formed at all three temperatures in the pentane and methanol systems. No azeotropes appear in the other three systems.

Reduced Data

The y_i, γ_i, and G^E values obtained with the Mixon et al. data

Table XI. Calculated Data for the Dichloromethane (1) + Acetone (2) System at 348.16 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 69.32 COMPONENT 2 ■ 79.88

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	186.348	186.348	0.9671	0.9545	0.0	0.7088	1.0000	0.0
0.050	187.765	187.764	0.9668	0.9541	0.0569	0.7107	0.9999	-49.72
0.100	189.281	189.277	0.9664	0.9538	0.1141	0.7184	0.9989	-98.47
0.150	191.041	191.038	0.9660	0.9533	0.1730	0.7322	0.9962	-144.77
0.200	193.195	193.190	0.9655	0.9529	0.2340	0.7508	0.9908	-187.28
0.250	195.885	195.880	0.9649	0.9522	0.2973	0.7732	0.9824	-224.77
0.300	199.192	199.187	0.9642	0.9515	0.3617	0.7966	0.9713	-256.48
0.350	203.153	203.149	0.9634	0.9506	0.4263	0.8200	0.9578	-282.10
0.400	207.805	207.801	0.9625	0.9495	0.4902	0.8431	0.9420	-301.40
0.450	213.169	213.166	0.9615	0.9483	0.5526	0.8655	0.9239	-314.18
0.500	219.230	219.227	0.9603	0.9469	0.6124	0.8867	0.9039	-320.30
0.550	225.962	225.960	0.9591	0.9454	0.6691	0.9064	0.8822	-319.74
0.600	233.339	233.336	0.9577	0.9437	0.7221	0.9245	0.8589	-312.47
0.650	241.336	241.334	0.9562	0.9419	0.7713	0.9411	0.8338	-298.40
0.700	249.928	249.927	0.9546	0.9399	0.8164	0.9562	0.8067	-277.36
0.750	259.069	259.067	0.9530	0.9378	0.8574	0.9696	0.7776	-249.12
0.800	268.663	268.662	0.9512	0.9356	0.8940	0.9809	0.7471	-213.47
0.850	278.606	278.606	0.9494	0.9333	0.9264	0.9899	0.7155	-170.32
0.900	288.796	288.796	0.9476	0.9310	0.9547	0.9965	0.6827	-119.55
0.950	299.079	299.079	0.9457	0.9286	0.9791	1.0005	0.6505	-60.97
1.000	308.741	308.741	0.9440	0.9264	1.0000	1.0000	0.6879	0.0

Table XII. Calculated Data for the Dichloromethane (1) + Acetone (2) System at 398.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 75.79 COMPONENT 2 = 87.70

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	679.848	679.848	0.9172	0.8870	0.0	0.7799	1.0000	0.0
0.050	684.512	684.524	0.9164	0.8863	0.0559	0.7884	0.9997	-40.29
0.100	689.856	689.875	0.9155	0.8854	0.1126	0.7998	0.9985	-78.41
0.150	696.173	696.194	0.9144	0.8845	0.1706	0.8142	0.9959	-113.53
0.200	703.727	703.750	0.9132	0.8833	0.2298	0.8305	0.9917	-144.93
0.250	712.643	712.666	0.9119	0.8819	0.2897	0.8469	0.9861	-172.23
0.300	723.002	723.026	0.9104	0.8803	0.3499	0.8631	0.9790	-195.28
0.350	734.884	734.909	0.9087	0.8785	0.4100	0.8791	0.9704	-213.91
0.400	748.369	748.394	0.9069	0.8764	0.4694	0.8947	0.9602	-227.97
0.450	763.518	763.546	0.9049	0.8741	0.5277	0.9099	0.9484	-237.25
0.500	780.328	780.359	0.9026	0.8716	0.5844	0.9242	0.9351	-241.66
0.550	798.785	798.820	0.9002	0.8688	0.6390	0.9375	0.9204	-241.11
0.600	818.872	818.910	0.8976	0.8657	0.6912	0.9498	0.9043	-235.55
0.650	840.576	840.616	0.8948	0.8624	0.7407	0.9610	0.8867	-224.84
0.700	863.880	863.921	0.8919	0.8589	0.7875	0.9712	0.8675	-208.86
0.750	888.714	888.756	0.8887	0.8551	0.8311	0.9802	0.8467	-187.39
0.800	914.877	914.917	0.8855	0.8511	0.8714	0.9876	0.8250	-160.37
0.850	942.147	942.183	0.8820	0.8470	0.9084	0.9933	0.8029	-127.85
0.900	970.301	970.330	0.8785	0.8427	0.9420	0.9973	0.7809	-89.96
0.950	999.099	999.116	0.8750	0.8383	0.9724	0.9995	0.7599	-46.95
1.000	1028.080	1028.080	0.8714	0.8339	1.0000	1.0000	0.7489	0.0

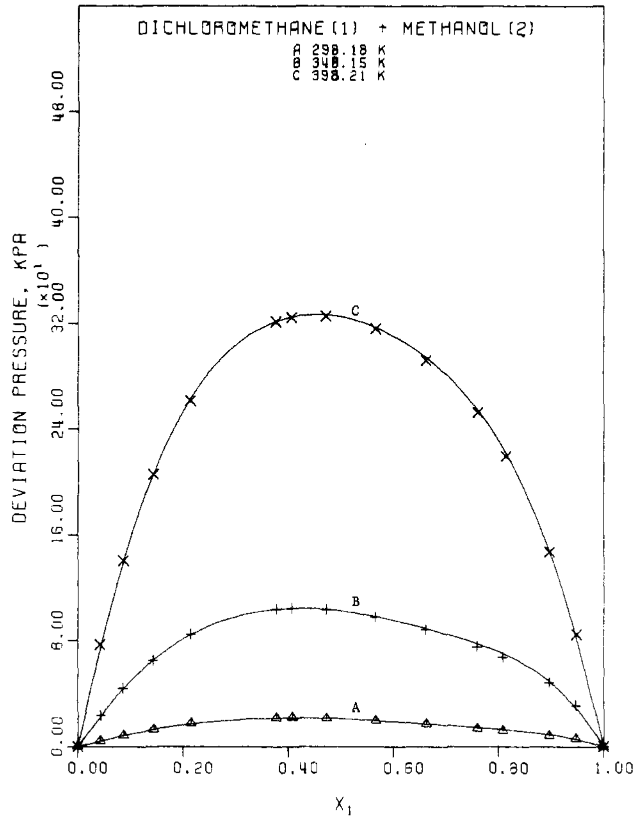

Figure 4. Deviation from Raoult's law for the system dichloromethane (1) + methanol (2). The $\times 10^1$ notation is explained in Figure 1.

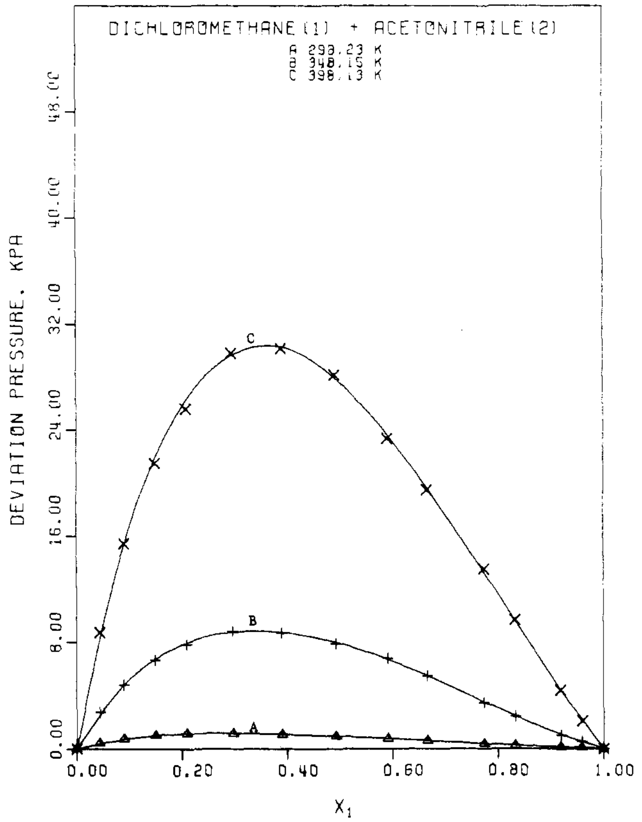

Figure 5. Deviation from Raoult's law for the system dichloromethane (1) + acetonitrile (2). The $\times 10^1$ notation is explained in Figure 1.

reduction method are given in Tables VII–XXI, which have been abbreviated from the 41 points actually used in the Mixon et al. data reduction method. The Peng–Robinson equation of state (*3*) was used to estimate the vapor-phase fugacity coefficients. The pure-compound parameters used for the Peng–Robinson equation are listed in Table XXII.

The "experimental" pressure values in Tables VII–XXI are from the splined fits of the experimental P vs. x_1 values. The "calculated" pressure values are from the Mixon et al. data reduction method. That method can usually be made to reproduce the input P values to any desired precision. In turn—as shown by Tables II–VI—the splined fits can reproduce smooth data very closely. Hence, the Mixon et al. method has the capability of fitting the experimental pressure data very closely.

The closeness with which the Barker (*4*) method reproduces the experimental P vs. x_1 values depends upon the G^E correlation used. Table XXIII summarizes the results obtained with six G^E equations for the dichloromethane + methanol system. Experience has shown that accuracy of the pressure fits increases, in general, with the number of constants in the G^E correlation. The Van Laar, Wilson, and UNIQUAC equations have two constants. The NRTL was used as a three-constant equation. The modified Margules (*5*) and Redlich–Kister equations have five constants. The five-constant Redlich–Kister equation usually will give the best results or be a close second insofar as the pressure fits are concerned. Also, it usually gives γ_i^∞ values which agree well with the Mixon et al. results. The five-constant Margules has the second-best record on the pressure fits but for this system it has trouble with the γ_2^∞ value. As usual, the various methods tend to agree much better on the γ_1^∞ values than on the γ_2^∞ values.

Table XIII. Calculated Data for the Dichloromethane (1) + Ethyl Acetate (2) System at 298.21 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 64.49 COMPONENT 2 = 98.43

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	12.674	12.674	0.9970	0.9935	0.0	0.5681	1.0000	0.0
0.050	13.605	13.604	0.9967	0.9931	0.1134	0.5370	1.0012	-74.22
0.100	14.523	14.522	0.9964	0.9926	0.2134	0.5391	1.0004	-152.34
0.150	15.615	15.614	0.9960	0.9921	0.3140	0.5682	0.9927	-225.63
0.200	16.891	16.890	0.9956	0.9915	0.4099	0.6015	0.9808	-290.50
0.250	18.330	18.329	0.9952	0.9908	0.4974	0.6334	0.9662	-346.97
0.300	19.946	19.945	0.9947	0.9901	0.5766	0.6655	0.9482	-395.14
0.350	21.761	21.761	0.9942	0.9892	0.6477	0.6987	0.9263	-434.65
0.400	23.798	23.797	0.9936	0.9883	0.7108	0.7332	0.8997	-464.91
0.450	26.067	26.066	0.9929	0.9873	0.7661	0.7689	0.8687	-485.21
0.500	28.549	28.549	0.9922	0.9862	0.8133	0.8040	0.8343	-495.10
0.550	31.221	31.221	0.9915	0.9850	0.8530	0.8376	0.7973	-494.35
0.600	34.057	34.057	0.9907	0.9837	0.8859	0.8691	0.7585	-482.87
0.650	37.030	37.030	0.9899	0.9823	0.9129	0.8981	0.7181	-460.59
0.700	40.111	40.110	0.9891	0.9809	0.9350	0.9243	0.6764	-427.40
0.750	43.268	43.268	0.9882	0.9795	0.9529	0.9475	0.6336	-383.16
0.800	46.470	46.470	0.9873	0.9780	0.9673	0.9675	0.5895	-327.58
0.850	49.659	49.658	0.9865	0.9765	0.9787	0.9836	0.5453	-260.31
0.900	52.736	52.736	0.9856	0.9751	0.9876	0.9946	0.5049	-181.59
0.950	55.611	55.611	0.9848	0.9738	0.9945	0.9996	0.4753	-93.11
1.000	58.283	58.283	0.9841	0.9726	1.0000	1.0000	0.4802	0.0

Table XIV. Calculated Data for the Dichloromethane (1) + Ethyl Acetate (2) System at 348.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 69.32 COMPONENT 2 = 105.54

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	94.732	94.732	0.9852	0.9683	0.0	0.6331	1.0000	0.0
0.050	99.378	99.377	0.9840	0.9668	0.0926	0.6252	1.0002	-67.47
0.100	104.249	104.246	0.9828	0.9652	0.1808	0.6390	0.9981	-134.51
0.150	109.924	109.921	0.9815	0.9634	0.2695	0.6688	0.9916	-195.44
0.200	116.351	116.348	0.9801	0.9615	0.3548	0.6977	0.9828	-248.62
0.250	123.393	123.390	0.9786	0.9594	0.4341	0.7230	0.9727	-294.84
0.300	131.110	131.106	0.9770	0.9571	0.5079	0.7477	0.9604	-334.46
0.350	139.600	139.596	0.9752	0.9546	0.5764	0.7729	0.9451	-367.21
0.400	148.963	148.960	0.9734	0.9518	0.6397	0.7992	0.9263	-392.54
0.450	159.261	159.258	0.9714	0.9488	0.6976	0.8263	0.9037	-409.76
0.500	170.450	170.448	0.9693	0.9456	0.7494	0.8530	0.8780	-418.36
0.550	182.464	182.462	0.9670	0.9421	0.7953	0.8786	0.8498	-418.07
0.600	195.235	195.233	0.9646	0.9384	0.8353	0.9026	0.8193	-408.68
0.650	208.678	208.677	0.9622	0.9345	0.8699	0.9248	0.7868	-390.00
0.700	222.657	222.656	0.9596	0.9305	0.8995	0.9446	0.7529	-361.93
0.750	237.034	237.033	0.9570	0.9263	0.9246	0.9618	0.7180	-324.39
0.800	251.668	251.667	0.9543	0.9221	0.9458	0.9761	0.6822	-277.35
0.850	266.391	266.390	0.9516	0.9178	0.9634	0.9875	0.6459	-220.74
0.900	280.994	280.994	0.9490	0.9135	0.9781	0.9956	0.6099	-154.63
0.950	295.237	295.237	0.9464	0.9094	0.9901	1.0001	0.5765	-79.40
1.000	308.539	308.539	0.9440	0.9055	1.0000	1.0000	0.6058	0.0

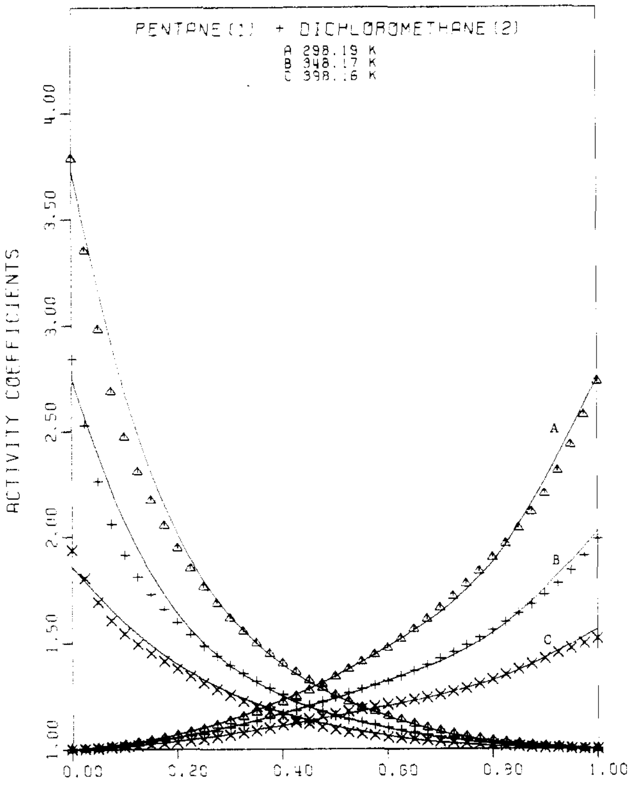

Figure 6. Activity coefficients for the pentane (1) + dichloromethane (2) system. Curves are from Barker method, points from Mixon et al. method.

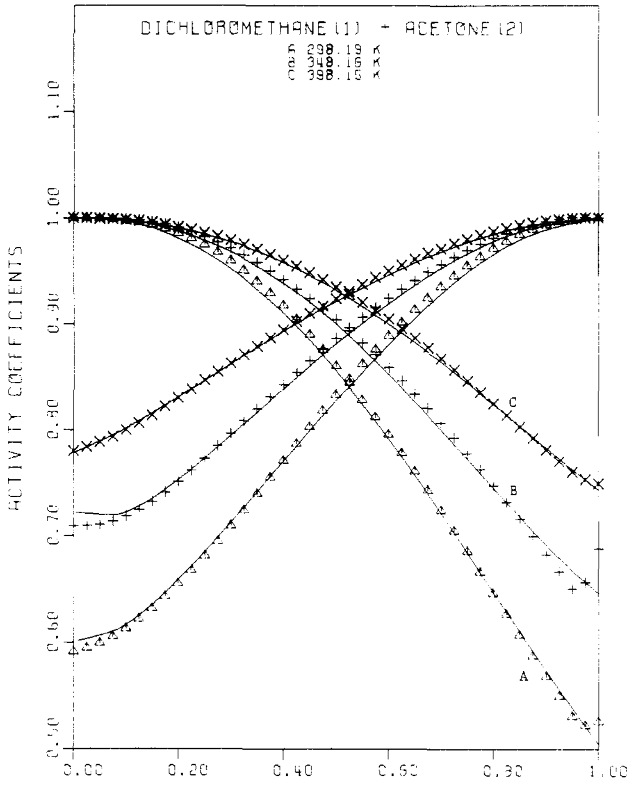

Figure 7. Activity coefficients for the dichloromethane (1) + acetone (2) system. Curves are from Barker method, points from Mixon et al. method.

Table XXIV gives a more complete comparison of the pressure fits provided by the two data reduction methods. The Barker results shown there are for the five-constant Redlich–Kister G^E correlation.

Figures 6–10 compare the activity coefficients provided by the Mixon et al. and Barker methods. Again, the Barker results are based on the Redlich–Kister equation. The points represent the Mixon et al. results and are accurately positioned, but the curves only approximate the Barker results. The curves are drawn by the plotting software and the fitting routine used there is not sophisticated enough to reproduce the input data exactly when there are sharp bends in the curves.

The difficulty of measuring accurate data for almost ideal systems is illustrated by the right end of the activity coefficient curve for the dichloromethane (1) + acetonitrile (2) system at 298.23 in Figure 10. The P vs. x_1 data plotted smoothly (not shown) and the P_D vs. x_1 plot in Figure 5 appears satisfactory. The P_D/x_1x_2 plot in Figure 11 appears to be good enough although the last point at $x_1 = 0.9593$ appears suspicious. Only the x_1x_2/P_D plot in Figure 12 makes it obvious that trouble will be encountered with the activity coefficients at high x_1 values in the data reduction. The obviously bad point at $x_1 = 0.9593$ in Figure 12 is based on a measured pressure of 56.4267 kPa (423.235 mmHg). A decrease in that measured value of 0.1% would give an x_1x_2/P_D value of 4.275 which falls off the plot in Figure 12. A decrease of only 0.011% (0.047 mmHg) would be sufficient to bring the $x_1 = 0.9593$ point into line with the other points in Figure 12. Hence, uncertainties in the measured

Table XV. Calculated Data for the Dichloromethane (1) + Ethyl Acetate (2) System at 398.17 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 75.79 COMPONENT 2 = 114.85

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	393.481	393.481	0.9578	0.9107	0.0	0.7458	1.0000	0.0
0.050	409.158	409.154	0.9549	0.9072	0.0818	0.7236	1.0006	-51.54
0.100	424.731	424.724	0.9521	0.9039	0.1592	0.7283	0.9998	-105.53
0.150	442.430	442.420	0.9491	0.9002	0.2376	0.7524	0.9951	-155.09
0.200	462.161	462.148	0.9459	0.8961	0.3140	0.7758	0.9887	-198.18
0.250	483.479	483.465	0.9425	0.8918	0.3863	0.7956	0.9815	-235.57
0.300	506.501	506.489	0.9391	0.8873	0.4549	0.8144	0.9728	-267.68
0.350	531.454	531.445	0.9354	0.8824	0.5199	0.8334	0.9621	-294.32
0.400	558.565	558.562	0.9316	0.8772	0.5813	0.8529	0.9488	-315.08
0.450	587.990	587.992	0.9275	0.8715	0.6388	0.8727	0.9328	-329.45
0.500	619.677	619.686	0.9232	0.8655	0.6921	0.8920	0.9145	-337.04
0.550	653.540	653.557	0.9187	0.8591	0.7409	0.9104	0.8941	-337.64
0.600	689.495	689.517	0.9140	0.8524	0.7852	0.9275	0.8718	-331.04
0.650	727.425	727.453	0.9091	0.8453	0.8251	0.9433	0.8477	-317.10
0.700	767.154	767.185	0.9040	0.8378	0.8607	0.9574	0.8219	-295.65
0.750	808.501	808.533	0.8988	0.8301	0.8924	0.9698	0.7944	-266.53
0.800	851.282	851.312	0.8934	0.8221	0.9204	0.9804	0.7651	-229.55
0.850	895.311	895.340	0.8879	0.8139	0.9449	0.9892	0.7335	-184.35
0.900	940.115	940.138	0.8823	0.8055	0.9662	0.9958	0.7004	-130.48
0.950	984.793	984.809	0.8767	0.7972	0.9844	0.9994	0.6699	-68.12
1.000	1028.408	1028.408	0.8713	0.7891	1.0000	1.0000	0.6638	0.0

Table XVI. Calculated Data for Dichloromethane (1) + Methanol (2) System at 298.18 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 64.49 COMPONENT 2 = 40.81

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	16.996	16.996	0.9954	0.9957	0.0	2.9379	1.0000	0.0
0.050	24.218	24.219	0.9934	0.9939	0.3311	2.7844	1.0014	130.16
0.100	30.742	30.743	0.9916	0.9922	0.4979	2.6525	1.0053	253.62
0.150	36.648	36.649	0.9900	0.9907	0.5989	2.5311	1.0121	370.66
0.200	41.853	41.854	0.9886	0.9894	0.6653	2.4046	1.0232	480.60
0.250	46.264	46.265	0.9874	0.9883	0.7110	2.2692	1.0407	582.07
0.300	49.901	49.902	0.9864	0.9874	0.7436	2.1309	1.0659	673.49
0.350	52.851	52.851	0.9856	0.9866	0.7678	1.9955	1.1003	753.47
0.400	55.200	55.200	0.9849	0.9860	0.7862	1.8660	1.1456	820.77
0.450	57.036	57.036	0.9844	0.9856	0.8004	1.7441	1.2044	874.12
0.500	58.453	58.453	0.9841	0.9852	0.8118	1.6308	1.2800	912.24
0.550	59.545	59.545	0.9838	0.9849	0.8211	1.5270	1.3766	933.83
0.600	60.404	60.404	0.9835	0.9847	0.8292	1.4336	1.4996	937.63
0.650	61.082	61.081	0.9833	0.9845	0.8365	1.3497	1.6586	922.28
0.700	61.604	61.604	0.9832	0.9844	0.8433	1.2741	1.8703	886.00
0.750	61.998	61.998	0.9831	0.9843	0.8499	1.2060	2.1627	826.39
0.800	62.286	62.286	0.9830	0.9842	0.8571	1.1454	2.5855	740.25
0.850	62.457	62.457	0.9830	0.9842	0.8663	1.0925	3.2346	622.97
0.900	62.487	62.487	0.9830	0.9842	0.8802	1.0488	4.3498	470.86
0.950	61.820	61.820	0.9831	0.9844	0.9049	1.0108	6.8338	263.57
1.000	58.191	58.191	0.9841	0.9853	1.0000	1.0000	10.3221	0.0

Table XVII. Calculated Data for Dichloromethane (1) + Methanol (2) System at 348.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 69.41 COMPONENT 2 = 44.16

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	151.267	151.267	0.9726	0.9754	0.0	2.9557	1.0000	0.0
0.050	186.206	186.211	0.9662	0.9698	0.2219	2.7515	1.0018	151.57
0.100	216.304	216.309	0.9607	0.9649	0.3583	2.5635	1.0076	292.32
0.150	241.981	241.986	0.9561	0.9608	0.4502	2.3892	1.0179	421.72
0.200	263.643	263.647	0.9522	0.9573	0.5160	2.2273	1.0332	539.14
0.250	281.695	281.698	0.9489	0.9544	0.5652	2.0773	1.0543	643.90
0.300	296.538	296.540	0.9462	0.9520	0.6031	1.9385	1.0824	735.25
0.350	308.577	308.578	0.9440	0.9501	0.6332	1.8104	1.1187	812.36
0.400	318.214	318.215	0.9423	0.9485	0.6575	1.6929	1.1647	874.38
0.450	325.829	325.830	0.9409	0.9473	0.6777	1.5855	1.2226	920.37
0.500	331.779	331.779	0.9398	0.9463	0.6949	1.4879	1.2951	949.35
0.550	336.417	336.417	0.9390	0.9456	0.7101	1.4002	1.3852	960.29
0.600	340.079	340.079	0.9383	0.9450	0.7244	1.3226	1.4963	952.25
0.650	342.875	342.876	0.9378	0.9446	0.7384	1.2540	1.6355	924.28
0.700	344.785	344.785	0.9375	0.9443	0.7523	1.1924	1.8166	874.88
0.750	345.783	345.782	0.9373	0.9441	0.7666	1.1371	2.0596	801.72
0.800	345.761	345.761	0.9373	0.9441	0.7845	1.0908	2.3773	702.55
0.850	344.022	344.022	0.9376	0.9444	0.8101	1.0552	2.7798	576.13
0.900	339.613	339.612	0.9384	0.9452	0.8454	1.0276	3.3543	421.35
0.950	330.113	330.113	0.9401	0.9467	0.8978	1.0070	4.3194	231.01
1.000	308.332	308.332	0.9440	0.9503	1.0000	1.0000	5.6729	0.0

Table XVIII. Calculated Data for Dichloromethane (1) + Methanol (2) System at 398.21 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 75.99 COMPONENT 2 = 48.61

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	737.122	737.122	0.9082	0.9207	0.0	2.9042	1.0000	0.0
0.050	840.954	840.949	0.8952	0.9097	0.1534	2.5847	1.0030	166.51
0.100	923.961	923.952	0.8848	0.9009	0.2560	2.3380	1.0111	313.94
0.150	992.345	992.333	0.8763	0.8937	0.3316	2.1440	1.0236	444.46
0.200	1048.157	1048.147	0.8694	0.8878	0.3896	1.9769	1.0414	558.74
0.250	1093.014	1093.008	0.8638	0.8830	0.4353	1.8291	1.0652	656.60
0.300	1128.534	1128.531	0.8593	0.8793	0.4724	1.6977	1.0958	737.64
0.350	1156.336	1156.337	0.8559	0.8764	0.5034	1.5815	1.1338	801.47
0.400	1178.021	1178.025	0.8531	0.8741	0.5304	1.4799	1.1799	847.77
0.450	1194.747	1194.755	0.8510	0.8724	0.5548	1.3916	1.2348	876.43
0.500	1207.200	1207.213	0.8495	0.8711	0.5776	1.3148	1.3000	887.29
0.550	1216.044	1216.057	0.8484	0.8702	0.6002	1.2492	1.3755	880.19
0.600	1221.850	1221.865	0.8476	0.8696	0.6251	1.1971	1.4569	855.75
0.650	1224.187	1224.201	0.8473	0.8694	0.6507	1.1519	1.5541	815.23
0.700	1222.017	1222.031	0.8476	0.8697	0.6744	1.1071	1.6874	755.42
0.750	1214.289	1214.300	0.8485	0.8706	0.7043	1.0736	1.8296	676.29
0.800	1199.955	1199.965	0.8502	0.8722	0.7401	1.0476	1.9905	579.06
0.850	1177.781	1177.788	0.8529	0.8746	0.7824	1.0269	2.1874	463.51
0.900	1144.756	1144.760	0.8570	0.8782	0.8352	1.0118	2.4268	328.53
0.950	1096.880	1096.879	0.8629	0.8834	0.9047	1.0029	2.7062	173.91
1.000	1030.144	1030.144	0.8712	0.8906	1.0000	1.0000	3.0283	0.0

Table XIX. Calculated Data for Dichloromethane (1) + Acetonitrile (2) System at 298.23 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 64.50 COMPONENT 2 = 52.36

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	11.881	11.881	0.9970	0.9947	0.0	1.2018	1.0000	0.0
0.050	14.680	14.680	0.9962	0.9935	0.2297	1.1733	1.0006	21.27
0.100	17.342	17.341	0.9954	0.9924	0.3803	1.1464	1.0025	39.46
0.150	19.874	19.873	0.9947	0.9913	0.4871	1.1210	1.0057	54.51
0.200	22.293	22.292	0.9940	0.9903	0.5672	1.0974	1.0103	66.35
0.250	24.632	24.631	0.9934	0.9893	0.6305	1.0774	1.0157	75.09
0.300	26.929	26.929	0.9927	0.9883	0.6825	1.0618	1.0213	81.09
0.350	29.215	29.215	0.9921	0.9874	0.7265	1.0504	1.0265	84.87
0.400	31.492	31.491	0.9914	0.9865	0.7644	1.0416	1.0317	86.86
0.450	33.755	33.755	0.9908	0.9855	0.7973	1.0344	1.0370	87.28
0.500	36.002	36.002	0.9902	0.9846	0.8261	1.0281	1.0427	86.25
0.550	38.231	38.231	0.9896	0.9837	0.8515	1.0224	1.0492	83.77
0.600	40.446	40.446	0.9890	0.9828	0.8743	1.0173	1.0563	79.84
0.650	42.653	42.653	0.9884	0.9819	0.8948	1.0129	1.0640	74.45
0.700	44.856	44.856	0.9878	0.9810	0.9135	1.0091	1.0722	67.64
0.750	47.061	47.061	0.9872	0.9800	0.9307	1.0060	1.0809	59.42
0.800	49.274	49.274	0.9866	0.9791	0.9466	1.0037	1.0897	49.85
0.850	51.498	51.498	0.9860	0.9782	0.9613	1.0020	1.0983	39.03
0.900	53.742	53.742	0.9853	0.9773	0.9751	1.0010	1.1054	27.11
0.950	56.006	56.006	0.9847	0.9764	0.9880	1.0007	1.1092	14.44
1.000	58.247	58.247	0.9841	0.9755	1.0000	1.0000	1.1596	0.0

Table XX. Calculated Data for Dichloromethane (1) + Acetonitrile (2) System at 348.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 69.41 COMPONENT 2 = 55.91

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	82.110	82.110	0.9862	0.9760	0.0	1.2666	1.0000	0.0
0.050	96.452	96.449	0.9833	0.9718	0.1869	1.2253	1.0008	31.73
0.100	109.904	109.900	0.9807	0.9680	0.3195	1.1900	1.0032	58.67
0.150	122.695	122.691	0.9782	0.9644	0.4200	1.1609	1.0067	81.26
0.200	135.025	135.020	0.9759	0.9610	0.4999	1.1374	1.0111	100.05
0.250	146.978	146.973	0.9736	0.9577	0.5655	1.1175	1.0163	115.42
0.300	158.607	158.603	0.9715	0.9545	0.6206	1.1001	1.0223	127.59
0.350	169.969	169.964	0.9693	0.9514	0.6679	1.0848	1.0292	136.69
0.400	181.118	181.114	0.9673	0.9484	0.7092	1.0714	1.0369	142.84
0.450	192.096	192.093	0.9652	0.9454	0.7458	1.0597	1.0454	146.18
0.500	202.924	202.920	0.9633	0.9425	0.7785	1.0493	1.0548	146.78
0.550	213.615	213.611	0.9613	0.9397	0.8081	1.0400	1.0652	144.67
0.600	224.186	224.182	0.9593	0.9368	0.8352	1.0316	1.0769	139.83
0.650	234.656	234.654	0.9574	0.9341	0.8601	1.0242	1.0900	132.22
0.700	245.060	245.058	0.9555	0.9313	0.8833	1.0177	1.1045	121.78
0.750	255.434	255.432	0.9536	0.9286	0.9050	1.0121	1.1204	108.51
0.800	265.812	265.811	0.9517	0.9258	0.9256	1.0077	1.1377	92.37
0.850	276.231	276.230	0.9499	0.9231	0.9453	1.0042	1.1561	73.39
0.900	286.721	286.719	0.9480	0.9203	0.9642	1.0019	1.1755	51.63
0.950	297.303	297.302	0.9460	0.9176	0.9824	1.0005	1.1959	27.14
1.000	308.000	308.000	0.9441	0.9148	1.0000	1.0000	1.2170	0.0

Table XXI. Calculated Data for Dichloromethane (1) + Acetonitrile (2) System at 398.13 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 75.98 COMPONENT 2 = 60.38

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	336.597	336.597	0.9609	0.9324	0.0	1.2932	1.0000	0.0
0.050	380.790	380.784	0.9548	0.9237	0.1508	1.2457	1.0009	39.34
0.100	422.060	422.052	0.9491	0.9157	0.2654	1.2065	1.0035	72.58
0.150	461.366	461.360	0.9438	0.9081	0.3573	1.1760	1.0071	100.53
0.200	499.505	499.499	0.9387	0.9009	0.4340	1.1528	1.0114	124.12
0.250	536.643	536.641	0.9338	0.8940	0.4995	1.1333	1.0164	143.93
0.300	572.800	572.801	0.9291	0.8873	0.5561	1.1157	1.0224	160.17
0.350	607.995	607.999	0.9245	0.8808	0.6058	1.0994	1.0297	172.82
0.400	642.248	642.256	0.9201	0.8745	0.6499	1.0841	1.0384	181.82
0.450	675.632	675.644	0.9158	0.8684	0.6896	1.0698	1.0487	187.04
0.500	708.336	708.350	0.9116	0.8625	0.7258	1.0568	1.0603	188.41
0.550	740.561	740.576	0.9075	0.8568	0.7594	1.0453	1.0732	185.94
0.600	772.509	772.526	0.9034	0.8511	0.7908	1.0355	1.0870	179.73
0.650	804.322	804.338	0.8994	0.8454	0.8206	1.0273	1.1015	169.93
0.700	836.013	836.031	0.8954	0.8399	0.8488	1.0204	1.1171	156.67
0.750	867.578	867.594	0.8914	0.8343	0.8759	1.0145	1.1342	139.96
0.800	899.014	899.030	0.8874	0.8289	0.9018	1.0096	1.1535	119.73
0.850	930.318	930.331	0.8835	0.8235	0.9270	1.0054	1.1760	95.77
0.900	961.583	961.592	0.8796	0.8182	0.9515	1.0023	1.2020	67.78
0.950	993.038	993.043	0.8757	0.8128	0.9758	1.0005	1.2293	35.65
1.000	1024.922	1024.922	0.8717	0.8075	1.0000	1.0000	1.2493	0.0

Table XXII. Parameters for Peng-Robinson Equation[a]

component	T_c, K	P_c, MPa	ω
dichloromethane	510.15	6.080	0.1990
pentane	469.50	3.374	0.2067
acetone	508.10	4.700	0.3040
ethyl acetate	523.30	3.830	0.2030
methanol	512.64	8.092	0.5560
acetonitrile	545.50	4.830	0.3270

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

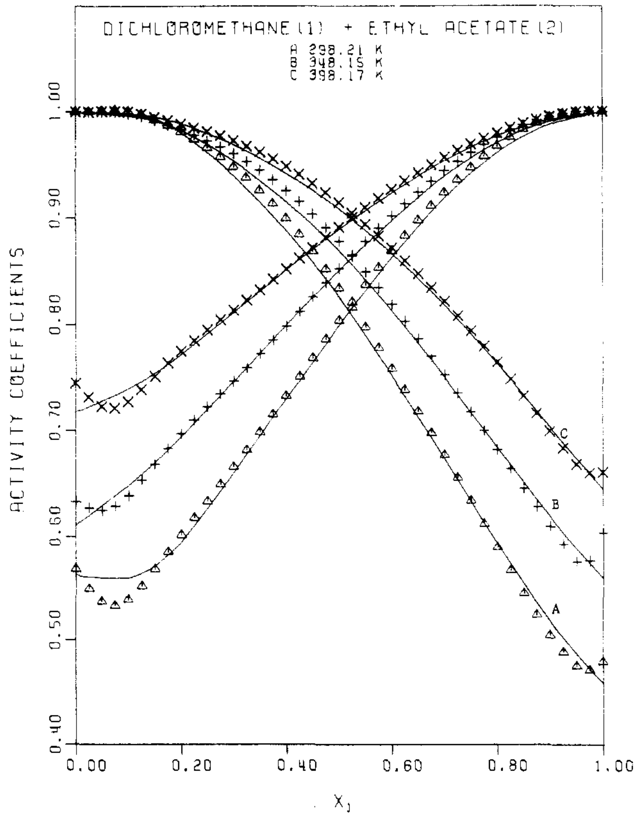

Figure 8. Activity coefficients for the dichloromethane (1) + ethyl acetate (2) system. Curves are from Barker method, points from Mixon et al. method.

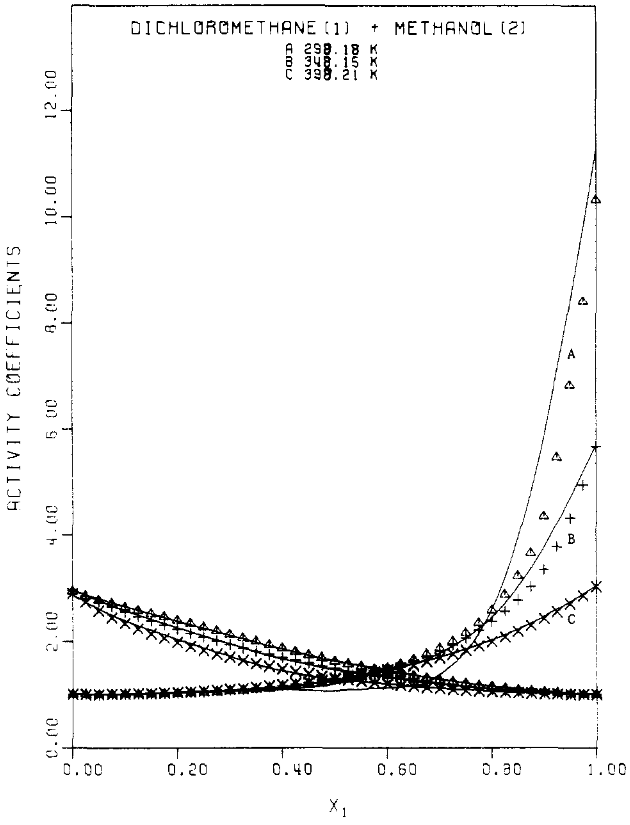

Figure 9. Activity coefficients for the dichloromethane (1) + methanol (2) system. Curves are from Barker method, points from Mixon et al. method.

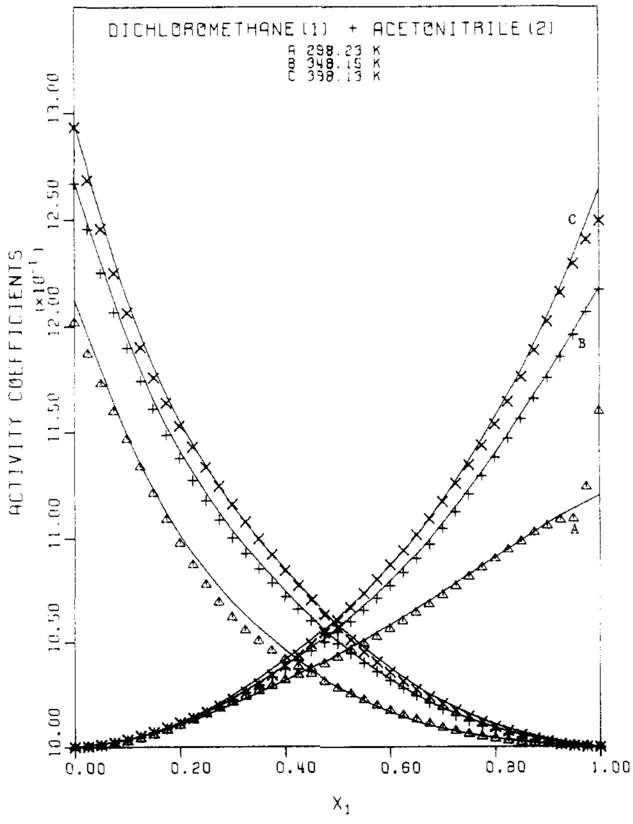

Figure 10. Activity coefficients for the dichloromethane (1) + acetonitrile (2) system. Curves are from Barker method, points from Mixon et al. method.

Table XXIII. Effect of Calculation Method on γ_i^∞ Values for the Dichloromethane (1) + Methanol (2) System

calculation method	accuracy of *P* fits, max % dev/rmsd[a]			calcd γ_i^∞ values					
				component 1			component 2		
	298.18 K	348.15 K	398.21 K	298.18 K	348.15 K	398.21 K	298.18 K	348.15 K	398.21 K
Mixon et al.	0.2/0.1	0.0/0.0	0.1/0.0	2.94	2.96	2.90	10.32	5.67	3.03
Barker:									
absolute Van Laar	0.7/0.4	0.3/0.1	0.1/0.0	2.97	2.93	2.83	9.70	5.40	3.02
Wilson	2.4/1.1	0.6/0.3	0.2/0.1	3.23	3.08	2.91	15.14	6.16	3.12
UNIQUAC	1.2/0.5	0.2/0.1	0.1/0.0	3.07	3.00	2.87	11.46	5.71	3.06
NRTL	0.8/0.4	0.2/0.1	0.1/0.0	3.02	2.98	2.85	10.10	5.54	3.04
modified Margules	0.7/0.3	0.0/0.0	0.1/0.0	2.80	2.95	2.85	20.96	5.88	3.18
Redlich-Kister	0.2/0.1	0.1/0.0	0.1/0.0	2.96	2.96	2.86	11.28	5.70	3.05

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

Table XXIV. Comparison of Barker and Mixon et al. Pressure Fits

temp, *K*	max % dev in *P*		rms for % dev	
	Barker	Mixon	Barker	Mixon
Pentane (1) + Dichloromethane (2)				
298.19	0.219	0.091	0.087	0.041
348.17	0.170	0.072	0.079	0.038
398.16	0.211	0.056	0.125	0.033
Dichloromethane (1) + Acetone (2)				
298.19	0.089	0.082	0.043	0.033
348.16	0.070	0.062	0.037	0.025
398.15	0.026	0.025	0.012	0.011
Dichloromethane (1) + Ethyl Acetate (2)				
298.21	0.253	0.066	0.111	0.036
348.15	0.095	0.063	0.055	0.024
398.17	0.075	0.034	0.040	0.018
Dichloromethane (1) + Methanol (2)				
298.18	0.170	0.156	0.103	0.081
348.15	0.058	0.032	0.026	0.015
398.21	0.060	0.092	0.027	0.047
Dichloromethane (1) + Acetonitrile (2)				
298.23	0.073	0.024	0.036	0.014
348.15	0.069	0.061	0.031	0.027
398.13	0.048	0.042	0.023	0.020

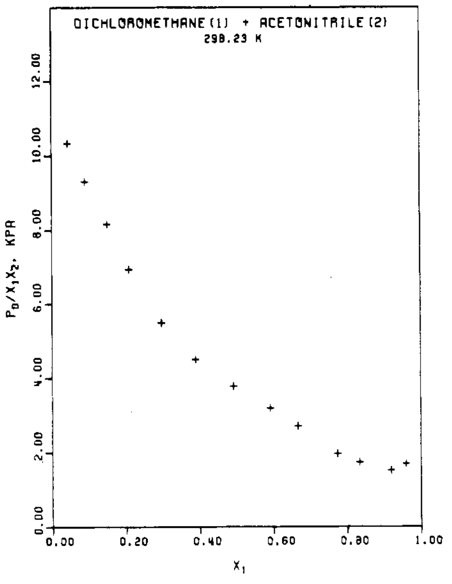

Figure 11. P_D/x_1x_2 plot for dichloromethane (1) + acetonitrile (2).

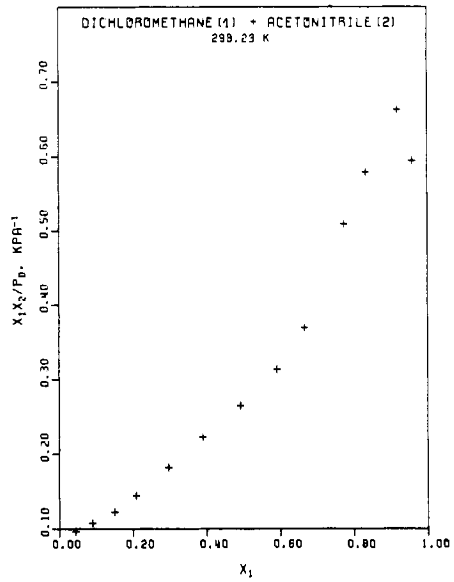

Figure 12. x_1x_2/P_D plot for dichlormethane (1) + acetonitrile (2).

pressure values of about 0.01% are sufficient to cause the anomalous points at the right end of the 298.23 K curve in Figure 10.

The scatter shown in the 298.23 K curve in Figure 10 could have been eliminated in either of two ways in the data reduction. The raw experimental pressure values above $x_1 = 0.7$ could have been adjusted by amounts in the 20–40-μm range to give a smooth x_1x_2/P_D plot, or the splined fits of the raw experimental data points could have been relaxed slightly and allowed to miss the experimental *P* values by larger amounts.

The sensitivity of the Mixon et al. method to the location of the experimental *P* values gives that method an advantage over the Barker method in the determination of γ_i^∞ values for highly nonideal systems which exhibit unusual behavior near the end points but, for a set of almost idea data such as the 298.23 K set in Figure 10, the Barker method is often more reliable.

Registry No. Dichloromethane, 75-09-2; pentane, 109-66-0; acetone, 67-64-1; ethyl acetate, 141-78-6; methanol, 67-56-1; acetonitrile, 75-05-8.

Literature Cited

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