sults. The Peng–Robinson equation of state was used for both the Mixon et al. and Barker methods. Table XIV lists the compound constants used for the Peng–Robinson equation. The binary interaction constant was set to 0.0 for all three binaries.

Registry No. Diethylamine, 109-89-7; methanol, 67-56-1; acetonitrile, 75-05-8; acetone, 67-64-1.

Literature Cited

(1) Maher, P. J.; Smith, B. D. *J. Chem. Eng. Data* **1979**, *24*, 16.
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(3) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
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Total Pressure Vapor–Liquid Equilibrium Data for Binary Systems of Dichloromethane with Benzene, Toluene, Nitromethane, and Chlorobenzene

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Total pressure vapor–liquid equilibrium (VLE) data are reported at 298 and 348 K for the binaries of dichloromethane with benzene and toluene and at 298, 348, and 398 K for dichloromethane with nitromethane and chlorobenzene. The experimental *PTx* data were reduced 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. Various equations of state were used to estimate 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 continuing effort to expand the vapor–liquid equilibrium data base for a general correlation of mixture properties. The apparatus and techniques for the experimental measurements—as well as the defining equation for the activity coefficient and the standard states used—were the same as described by Maher and Smith (*1*).

Chemicals Used

Table I lists the chemicals used and their stated purities. All chemicals were available in at least 99.9% purity. Activated molecular sieves (4 Å) were put into the containers with the chemicals as they were received. The chemicals were distilled through a Vigreux column (25-mm o.d. and 470-mm long) before they were loaded into the VLE cells. The first and last

Table I. Chemicals Used

component	vendor	purity, %
dichloromethane	Burdick and Jackson	99.9+
benzene	Burdick and Jackson	99.9+
toluene	Burdick and Jackson	99.9
nitromethane	Mallinckrodt	99.9
chlorobenzene	Burdick and Jackson	99.9+

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

298.15 K			348.00 K		
	P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	12.667	12.668	0.0	86.09	86.09
0.0547	14.866	14.863	0.0546	96.40	96.41
0.0781	15.791	15.786	0.0779	100.81	100.81
0.1091	17.004	17.016	0.1087	106.71	106.68
0.2045	20.939	20.936	0.2040	125.64	125.67
0.2999	25.080	25.068	0.2996	145.74	145.70
0.4443	31.61	31.64	0.4436	177.06	177.09
0.5461	36.46	36.44	0.5454	200.05	200.05
0.6299	40.44	40.44	0.6294	219.49	219.45
0.7144	44.47	44.49	0.7140	239.23	239.28
0.8094	49.02	49.01	0.8091	261.72	261.69
0.8715	51.95	51.95	0.8712	276.3	276.3
0.9250	54.47	54.47	0.9248	288.9	288.9
0.9678	56.49	56.48	0.9677	299.0	298.9
1.0000	57.99	57.99	1.0000	306.4	306.4

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

298.15 K			347.99 K		
	P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	3.920	3.921	0.0	32.71	32.71
0.0520	6.241	6.242	0.0517	44.51	44.51
0.0904	7.998	7.991	0.0897	53.37	53.34
0.1536	10.944	10.963	0.1526	68.35	68.39
0.2167	14.100	14.079	0.2159	84.17	84.17
0.3043	18.623	18.630	0.3038	107.07	107.00
0.4048	24.104	24.124	0.4042	134.02	134.09
0.5093	30.08	30.04	0.5084	163.13	163.12
0.6039	35.45	35.48	0.6032	190.27	190.24
0.7019	41.12	41.13	0.7015	218.88	218.90
0.7907	46.23	46.21	0.7899	244.95	244.93
0.8617	50.25	50.26	0.8613	265.93	265.95
0.9339	54.31	54.32	0.9337	287.2	287.1
0.9577	55.66	55.65	0.9576	294.1	294.1
1.0000	58.00	58.00	1.0000	306.5	306.5

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

298.05 K			347.99 K			398.13 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	4.808	4.814	0.0	41.95	41.97	0.0	203.11	203.21
0.0416	8.570	8.551	0.0413	59.38	59.30	0.0408	253.38	253.06
0.0827	11.906	11.927	0.0825	75.35	75.37	0.0819	300.3	300.4
0.1436	16.444	16.436	0.1432	97.07	97.18	0.1426	364.6	365.1
0.2112	20.891	20.898	0.2108	119.21	119.12	0.2103	431.6	431.1
0.3040	26.331	26.317	0.3036	146.24	146.21	0.3031	514.2	514.0
0.3997	31.26	31.27	0.3993	171.44	171.48	0.3981	592.6	593.1
0.4986	35.89	35.91	0.4983	195.51	195.52	0.4981	670.9	670.9
0.6106	40.83	40.83	0.6102	220.74	220.86	0.6096	752.3	751.4
0.6878	44.13	44.13	0.6874	237.94	237.65	0.6869	803.8	804.8
0.7832	48.10	48.10	0.7828	257.94	258.19	0.7824	870.0	869.5
0.8543	50.95	50.96	0.8540	273.80	273.69	0.8537	917.7	917.8
0.9160	53.37	53.36	0.9159	287.5	287.5	0.9156	960.6	960.8
0.9532	54.78	54.77	0.9531	296.0	296.0	0.9529	988.2	987.9
1.0000	56.52	56.52	1.0000	307.0	307.0	1.0000	1024.4	1024.4

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

298.03 K			347.97 K			398.10 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	1.682	1.682	0.0	16.212	16.223	0.0	84.12	84.81
0.0492	4.578	4.576	0.0483	30.23	30.17	0.0466	126.59	125.22
0.0765	6.158	6.163	0.0757	38.01	38.07	0.0745	149.04	149.45
0.1477	10.283	10.283	0.1468	58.47	58.47	0.1451	211.03	210.99
0.2175	14.303	14.298	0.2168	78.59	78.57	0.2154	272.19	272.76
0.3045	19.242	19.245	0.3041	103.60	103.60	0.3032	350.5	350.7
0.4036	24.809	24.814	0.4030	131.89	131.91	0.4008	439.1	438.5
0.4973	30.03	30.02	0.4966	158.72	158.71	0.4962	525.4	525.8
0.6012	35.74	35.75	0.6001	188.56	188.52	0.5998	622.7	622.6
0.7020	41.29	41.28	0.7016	217.96	218.00	0.7006	718.5	718.7
0.7891	46.06	46.06	0.7888	243.56	243.55	0.7876	803.3	803.1
0.8575	49.81	49.81	0.8572	263.73	263.70	0.8565	870.7	870.9
0.9171	53.12	53.11	0.9169	281.4	281.4	0.9164	931.8	931.8
0.9579	55.39	55.39	0.9577	293.6	293.6	0.9575	976.7	976.7
1.0000	57.78	57.78	1.0000	306.4	306.4	1.0000	1024.8	1024.8

Table VI. Calculated Data for the Dichloromethane (1) + Benzene (2) System at 298.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 64.81 COMPONENT 2 = 89.41

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	12.668	12.668	0.9968	0.9945	0.0	0.9324	1.0000	0.0
0.050	14.675	14.675	0.9962	0.9936	0.1788	0.9172	1.0004	-9.81
0.100	16.652	16.652	0.9956	0.9928	0.3135	0.9117	1.0008	-21.16
0.150	18.670	18.670	0.9950	0.9919	0.4216	0.9158	1.0001	-32.54
0.200	20.748	20.748	0.9944	0.9910	0.5106	0.9238	0.9982	-42.84
0.250	22.882	22.882	0.9938	0.9902	0.5848	0.9328	0.9954	-51.69
0.300	25.070	25.070	0.9932	0.9893	0.6472	0.9420	0.9917	-58.91
0.350	27.308	27.307	0.9926	0.9883	0.7003	0.9510	0.9871	-64.40
0.400	29.588	29.588	0.9920	0.9874	0.7458	0.9595	0.9819	-68.14
0.450	31.906	31.905	0.9913	0.9865	0.7850	0.9673	0.9760	-70.12
0.500	34.253	34.252	0.9907	0.9855	0.8189	0.9743	0.9697	-70.38
0.550	36.622	36.621	0.9900	0.9845	0.8485	0.9805	0.9630	-68.96
0.600	39.008	39.007	0.9894	0.9836	0.8743	0.9858	0.9560	-65.93
0.650	41.402	41.401	0.9887	0.9826	0.8970	0.9902	0.9489	-61.37
0.700	43.797	43.795	0.9881	0.9816	0.9171	0.9937	0.9421	-55.41
0.750	46.186	46.184	0.9874	0.9807	0.9349	0.9962	0.9357	-48.20
0.800	48.566	48.565	0.9867	0.9797	0.9507	0.9980	0.9300	-39.92
0.850	50.936	50.936	0.9861	0.9787	0.9649	0.9992	0.9250	-30.75
0.900	53.298	53.297	0.9855	0.9778	0.9777	0.9998	0.9210	-20.86
0.950	55.649	55.649	0.9848	0.9768	0.9893	1.0000	0.9184	-10.46
1.000	57.993	57.993	0.9842	0.9759	1.0000	1.0000	0.9219	0.0

Table VII. Calculated Data for the Dichloromethane (1) + Benzene (2) System at 348.00 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 69.42 COMPONENT 2 = 95.32

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	86.087	86.087	0.9855	0.9747	0.0	0.9299	1.0000	0.0
0.050	95.547	95.546	0.9836	0.9720	0.1412	0.9218	1.0002	-11.26
0.100	105.013	105.011	0.9817	0.9693	0.2575	0.9217	1.0001	-23.26
0.150	114.769	114.766	0.9798	0.9665	0.3571	0.9293	0.9989	-34.51
0.200	124.857	124.853	0.9778	0.9637	0.4432	0.9390	0.9967	-44.06
0.250	135.218	135.215	0.9758	0.9609	0.5178	0.9482	0.9939	-51.77
0.300	145.796	145.791	0.9738	0.9580	0.5825	0.9563	0.9907	-57.70
0.350	156.539	156.535	0.9718	0.9550	0.6389	0.9631	0.9874	-62.04
0.400	167.440	167.435	0.9697	0.9521	0.6885	0.9690	0.9838	-64.93
0.450	178.499	178.494	0.9677	0.9491	0.7323	0.9743	0.9798	-66.44
0.500	189.716	189.712	0.9656	0.9461	0.7712	0.9791	0.9754	-66.57
0.550	201.091	201.087	0.9635	0.9430	0.8060	0.9837	0.9704	-65.31
0.600	212.617	212.613	0.9614	0.9399	0.8373	0.9879	0.9648	-62.62
0.650	224.262	224.259	0.9593	0.9368	0.8654	0.9916	0.9587	-58.46
0.700	235.987	235.984	0.9571	0.9337	0.8906	0.9947	0.9526	-52.88
0.750	247.757	247.754	0.9550	0.9306	0.9134	0.9971	0.9465	-45.96
0.800	259.545	259.542	0.9528	0.9274	0.9340	0.9989	0.9410	-37.86
0.850	271.329	271.327	0.9507	0.9243	0.9527	0.9999	0.9363	-28.75
0.900	283.089	283.088	0.9485	0.9212	0.9698	1.0004	0.9332	-18.92
0.950	294.802	294.802	0.9464	0.9181	0.9854	1.0004	0.9340	-8.84
1.000	306.446	306.446	0.9443	0.9150	1.0000	1.0000	0.9544	0.0

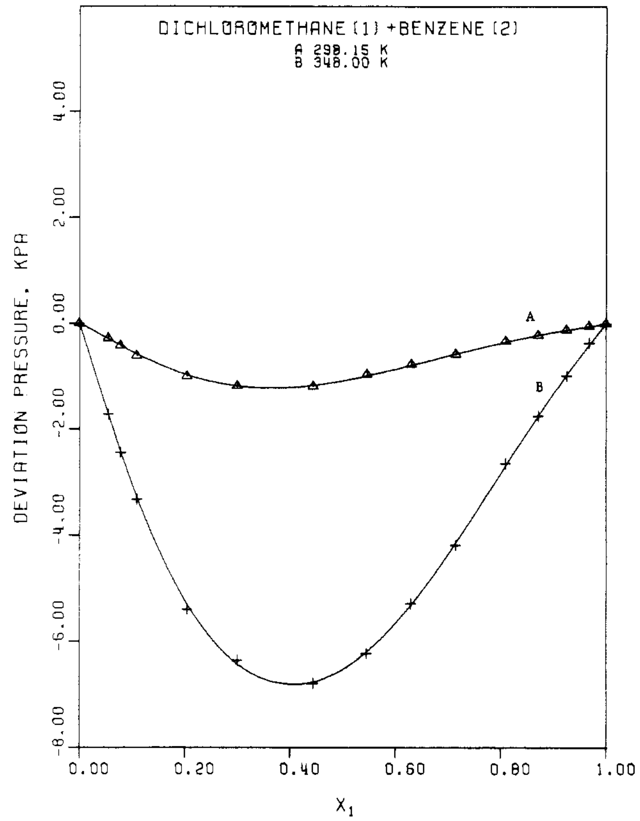

Figure 1. Deviations from Raoult's law for the dichloromethane (1) + benzene (2) system.

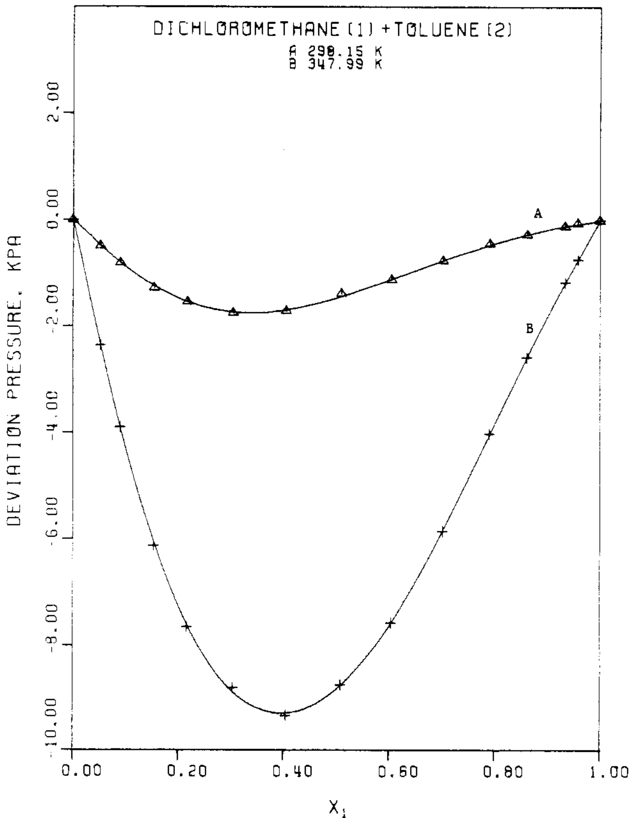

Figure 2. Deviations from Raoult's law for the dichloromethane (1) + toluene (2) system.

portions of the distillate were discarded. The retained samples were backflushed with nitrogen and put into amber glass bottles for transfer to the loading operation. The initial purity of each chemical was verified chromatographically. None of the com-

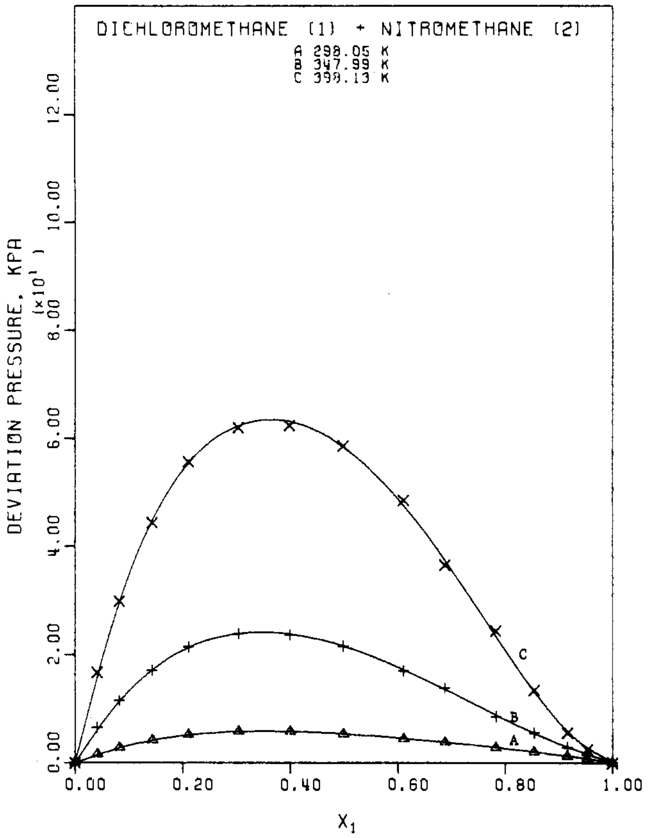

Figure 3. Deviations from Raoult's law for the dichloromethane (1) + nitromethane (2) system. The ordinate values run from 0.0 to 120.0.

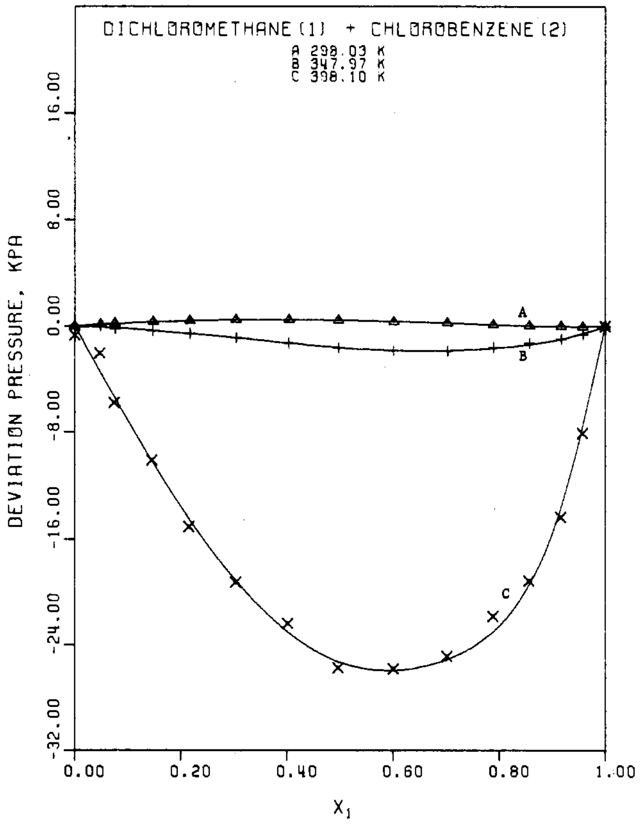

Figure 4. Deviations from Raoult's law for the dichloromethane (1) + chlorobenzene (2) system.

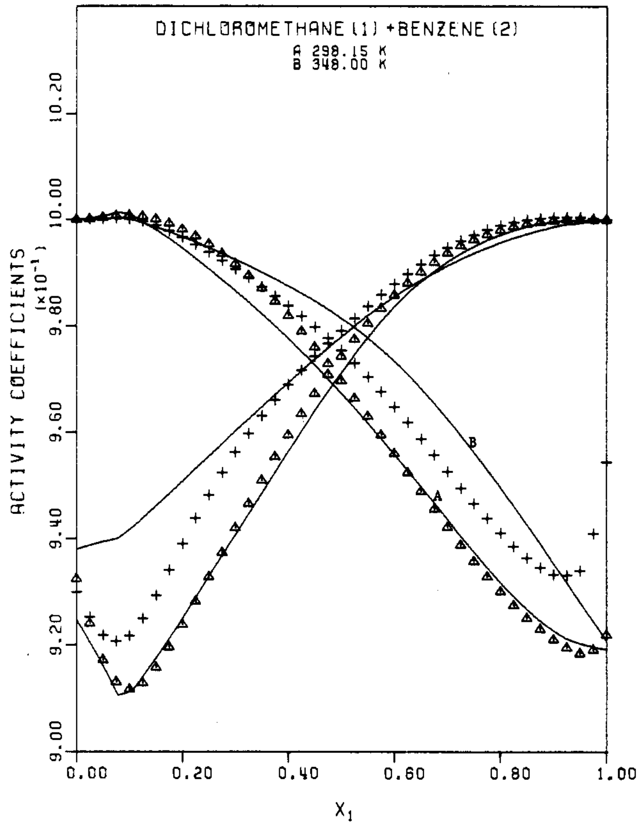

Figure 5. Activity coefficients for the dichloromethane (1) + benzene (2) system: curves from Barker results; points from Mixon et al. method. The ordinate values run from 0.9 to 1.020.

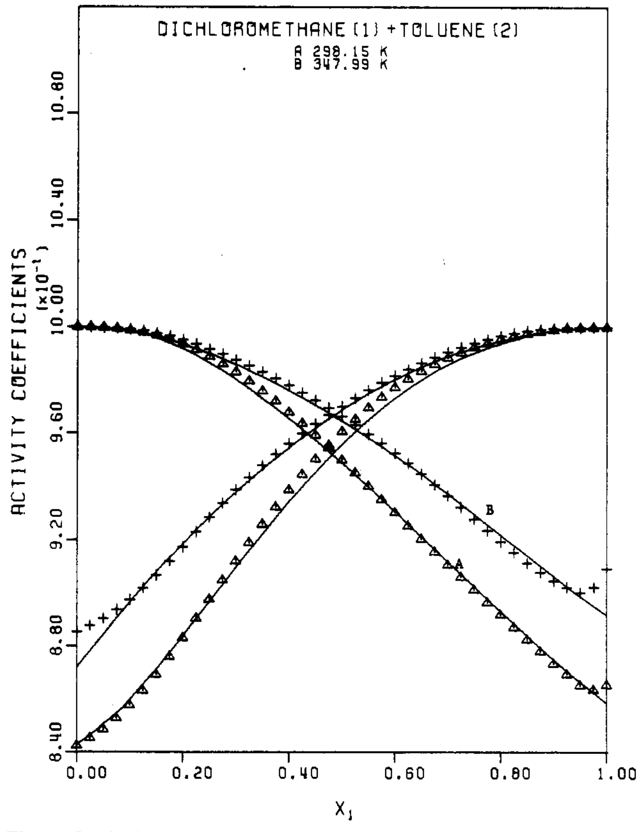

Figure 6. Activity coefficients for the dichloromethane (1) + toluene (2) system: curves from Barker results; points from Mixon et al. method. The ordinate values run from 0.840 to 1.060.

pounds exhibited any degradation during the experimental measurements; the cell pressures were stable with respect to time, and all liquids were perfectly clear when removed from the cells at the end of the last isotherm.

Table VIII. Calculated Data for the Dichloromethane (1) + Toluene (2) System at 298.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 64.81 COMPONENT 2 = 106.90

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	3.921	3.921	0.9992	0.9976	0.0	0.8425	1.0000	0.0
0.050	6.152	6.152	0.9985	0.9964	0.3939	0.8489	0.9998	-20.79
0.100	8.435	8.435	0.9978	0.9951	0.5810	0.8578	0.9989	-40.44
0.150	10.791	10.791	0.9971	0.9938	0.6908	0.8693	0.9970	-58.44
0.200	13.240	13.240	0.9964	0.9925	0.7633	0.8831	0.9936	-74.28
0.250	15.779	15.779	0.9957	0.9912	0.8144	0.8977	0.9889	-87.60
0.300	18.400	18.400	0.9950	0.9898	0.8521	0.9120	0.9830	-98.25
0.350	21.096	21.095	0.9943	0.9884	0.8809	0.9258	0.9759	-106.17
0.400	23.854	23.853	0.9935	0.9869	0.9034	0.9386	0.9679	-111.35
0.450	26.661	26.661	0.9927	0.9855	0.9214	0.9502	0.9592	-113.83
0.500	29.506	29.506	0.9920	0.9840	0.9359	0.9606	0.9498	-113.70
0.550	32.376	32.375	0.9912	0.9825	0.9479	0.9696	0.9401	-111.07
0.600	35.258	35.257	0.9904	0.9810	0.9579	0.9772	0.9302	-106.08
0.650	38.140	38.140	0.9896	0.9794	0.9662	0.9834	0.9204	-98.89
0.700	41.018	41.017	0.9888	0.9779	0.9733	0.9884	0.9107	-89.70
0.750	43.888	43.888	0.9880	0.9764	0.9794	0.9924	0.9012	-78.64
0.800	46.747	46.746	0.9872	0.9749	0.9847	0.9955	0.8918	-65.83
0.850	49.591	49.590	0.9865	0.9734	0.9893	0.9977	0.8825	-51.40
0.900	52.416	52.416	0.9857	0.9720	0.9933	0.9991	0.8735	-35.46
0.950	55.220	55.220	0.9849	0.9705	0.9968	0.9999	0.8653	-18.16
1.000	57.997	57.997	0.9842	0.9690	1.0000	1.0000	0.8655	0.0

Table IX. Calculated Data for the Dichloromethane (1) + Toluene (2) System at 347.99 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 69.42 COMPONENT 2 = 113.10

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	32.708	32.708	0.9955	0.9868	0.0	0.8852	1.0000	0.0
0.050	44.117	44.115	0.9930	0.9823	0.2923	0.8904	0.9998	-17.24
0.100	55.768	55.765	0.9906	0.9780	0.4674	0.8974	0.9992	-33.45
0.150	67.753	67.750	0.9882	0.9737	0.5845	0.9066	0.9977	-48.20
0.200	80.142	80.138	0.9858	0.9693	0.6686	0.9175	0.9952	-61.04
0.250	92.906	92.902	0.9834	0.9648	0.7315	0.9284	0.9917	-71.69
0.300	105.988	105.984	0.9809	0.9602	0.7801	0.9386	0.9877	-80.13
0.350	119.337	119.332	0.9784	0.9556	0.8185	0.9478	0.9831	-86.45
0.400	132.924	132.920	0.9759	0.9509	0.8496	0.9560	0.9780	-90.74
0.450	146.734	146.730	0.9734	0.9461	0.8751	0.9634	0.9724	-93.06
0.500	160.748	160.745	0.9708	0.9413	0.8964	0.9701	0.9663	-93.45
0.550	174.949	174.946	0.9682	0.9364	0.9144	0.9762	0.9597	-91.93
0.600	189.318	189.316	0.9656	0.9315	0.9298	0.9816	0.9525	-88.52
0.650	203.836	203.834	0.9629	0.9266	0.9431	0.9865	0.9447	-83.21
0.700	218.465	218.464	0.9603	0.9216	0.9546	0.9907	0.9364	-76.01
0.750	233.165	233.163	0.9576	0.9166	0.9647	0.9941	0.9279	-66.95
0.800	247.895	247.894	0.9549	0.9116	0.9735	0.9968	0.9194	-56.12
0.850	262.615	262.614	0.9522	0.9067	0.9813	0.9986	0.9114	-43.64
0.900	277.287	277.287	0.9496	0.9017	0.9882	0.9997	0.9046	-29.77
0.950	291.904	291.904	0.9469	0.8968	0.9944	1.0001	0.9003	-14.90
1.000	306.472	306.472	0.9443	0.8919	1.0000	1.0000	0.9093	0.0

Table X. Calculated Data for the Dichloromethane (1) + Nitromethane (2) System at 298.05 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 64.81 COMPONENT 2 = 53.94

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	4.814	4.814	0.9988	0.9980	0.0	1.7779	1.0000	0.0
0.050	9.266	9.267	0.9975	0.9962	0.5048	1.6793	1.0014	67.60
0.100	13.260	13.261	0.9964	0.9946	0.6702	1.5933	1.0057	128.11
0.150	16.879	16.879	0.9954	0.9931	0.7532	1.5178	1.0127	181.65
0.200	20.194	20.195	0.9945	0.9918	0.8038	1.4519	1.0223	228.44
0.250	23.253	23.253	0.9937	0.9905	0.8381	1.3932	1.0346	268.61
0.300	26.095	26.096	0.9929	0.9894	0.8632	1.3409	1.0497	302.20
0.350	28.761	28.762	0.9921	0.9883	0.8826	1.2942	1.0678	329.27
0.400	31.279	31.279	0.9915	0.9873	0.8983	1.2524	1.0890	349.85
0.450	33.673	33.674	0.9908	0.9864	0.9114	1.2150	1.1137	363.90
0.500	35.970	35.970	0.9902	0.9855	0.9226	1.1816	1.1421	371.40
0.550	38.193	38.193	0.9896	0.9846	0.9324	1.1520	1.1746	372.30
0.600	40.368	40.368	0.9890	0.9837	0.9413	1.1261	1.2113	366.56
0.650	42.517	42.517	0.9884	0.9828	0.9496	1.1036	1.2526	354.19
0.700	44.643	44.642	0.9878	0.9820	0.9572	1.0840	1.3002	335.09
0.750	46.736	46.735	0.9872	0.9812	0.9644	1.0665	1.3574	308.94
0.800	48.790	48.789	0.9867	0.9803	0.9712	1.0505	1.4302	274.98
0.850	50.795	50.795	0.9861	0.9795	0.9778	1.0357	1.5298	231.89
0.900	52.748	52.747	0.9856	0.9788	0.9843	1.0219	1.6822	177.21
0.950	54.652	54.652	0.9851	0.9780	0.9912	1.0094	1.9654	105.86
1.000	56.518	56.518	0.9846	0.9773	1.0000	1.0000	3.1843	0.0

Table XI. Calculated Data for the Dichloromethane (1) + Nitromethane (2) System at 347.99 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 69.42 COMPONENT 2 = 57.21

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	41.972	41.972	0.9927	0.9883	0.0	1.6251	1.0000	0.0
0.050	62.789	62.787	0.9888	0.9827	0.3603	1.5522	1.0012	66.84
0.100	81.883	81.881	0.9852	0.9775	0.5310	1.4856	1.0047	126.85
0.150	99.470	99.466	0.9820	0.9728	0.6313	1.4251	1.0107	179.99
0.200	115.758	115.754	0.9790	0.9685	0.6979	1.3703	1.0192	226.25
0.250	130.942	130.937	0.9762	0.9644	0.7458	1.3209	1.0301	265.65
0.300	145.216	145.211	0.9736	0.9607	0.7824	1.2768	1.0434	298.23
0.350	158.757	158.751	0.9711	0.9571	0.8116	1.2376	1.0592	324.08
0.400	171.667	171.661	0.9688	0.9537	0.8357	1.2025	1.0777	343.27
0.450	184.027	184.021	0.9665	0.9504	0.8562	1.1709	1.0991	355.79
0.500	195.916	195.910	0.9644	0.9473	0.8740	1.1423	1.1240	361.54
0.550	207.414	207.408	0.9623	0.9443	0.8898	1.1165	1.1527	360.42
0.600	218.600	218.595	0.9602	0.9414	0.9040	1.0933	1.1859	352.25
0.650	229.555	229.550	0.9583	0.9385	0.9172	1.0727	1.2242	336.84
0.700	240.364	240.360	0.9563	0.9357	0.9295	1.0546	1.2683	313.97
0.750	251.117	251.113	0.9543	0.9329	0.9414	1.0390	1.3191	283.39
0.800	261.901	261.897	0.9524	0.9301	0.9529	1.0259	1.3780	244.82
0.850	272.805	272.803	0.9504	0.9272	0.9643	1.0155	1.4465	197.93
0.900	283.915	283.913	0.9484	0.9244	0.9757	1.0076	1.5279	142.29
0.950	295.297	295.297	0.9463	0.9214	0.9875	1.0023	1.6302	77.13
1.000	307.013	307.013	0.9442	0.9184	1.0000	1.0000	1.8073	0.0

Table XII. Calculated Data for the Dichloromethane (1) + Nitromethane (2) System at 398.13 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 75.79 COMPONENT 2 = 61.03

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	203.215	203.215	0.9757	0.9610	0.0	1.5658	1.0000	0.0
0.050	263.895	263.886	0.9677	0.9496	0.2580	1.5010	1.0011	70.64
0.100	320.260	320.249	0.9603	0.9391	0.4117	1.4408	1.0044	134.04
0.150	372.645	372.632	0.9536	0.9294	0.5143	1.3848	1.0101	190.02
0.200	421.478	421.467	0.9474	0.9205	0.5883	1.3333	1.0183	238.43
0.250	467.450	467.443	0.9415	0.9121	0.6449	1.2875	1.0287	279.28
0.300	511.294	511.288	0.9360	0.9042	0.6904	1.2478	1.0409	312.81
0.350	553.636	553.633	0.9306	0.8965	0.7285	1.2137	1.0549	339.38
0.400	594.605	594.606	0.9255	0.8892	0.7610	1.1838	1.0708	359.28
0.450	634.176	634.178	0.9205	0.8821	0.7892	1.1565	1.0894	372.55
0.500	672.326	672.331	0.9157	0.8753	0.8140	1.1313	1.1114	379.01
0.550	709.088	709.097	0.9111	0.8687	0.8362	1.1078	1.1376	378.34
0.600	744.707	744.716	0.9066	0.8624	0.8565	1.0861	1.1685	370.14
0.650	779.470	779.480	0.9023	0.8563	0.8753	1.0665	1.2045	354.05
0.700	813.667	813.677	0.8980	0.8502	0.8933	1.0491	1.2464	329.76
0.750	847.563	847.572	0.8938	0.8443	0.9106	1.0340	1.2948	296.94
0.800	881.380	881.388	0.8896	0.8384	0.9277	1.0214	1.3511	255.24
0.850	915.334	915.341	0.8853	0.8325	0.9448	1.0111	1.4171	204.24
0.900	949.778	949.781	0.8811	0.8265	0.9623	1.0036	1.4932	143.43
0.950	985.729	985.729	0.8766	0.8203	0.9809	0.9999	1.5613	73.29
1.000	1024.413	1024.413	0.8718	0.8137	1.0000	1.0000	1.5150	0.0

Table XIII. Calculated Data for the Dichloromethane (1) + Chlorobenzene (2) System at 298.03 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 64.81 COMPONENT 2 = 112.56

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	1.682	1.682	0.9997	0.9989	0.0	1.0824	1.0000	0.0
0.050	4.620	4.620	0.9988	0.9971	0.6533	1.0617	1.0004	8.43
0.100	7.523	7.523	0.9980	0.9955	0.7978	1.0547	1.0009	15.26
0.150	10.416	10.416	0.9972	0.9938	0.8618	1.0506	1.0015	21.46
0.200	13.294	13.294	0.9964	0.9922	0.8978	1.0468	1.0022	27.13
0.250	16.153	16.153	0.9956	0.9906	0.9209	1.0428	1.0034	32.23
0.300	18.991	18.991	0.9948	0.9890	0.9370	1.0387	1.0049	36.68
0.350	21.811	21.810	0.9940	0.9874	0.9489	1.0346	1.0068	40.42
0.400	24.613	24.613	0.9933	0.9858	0.9580	1.0305	1.0092	43.41
0.450	27.400	27.400	0.9925	0.9842	0.9653	1.0266	1.0120	45.61
0.500	30.174	30.173	0.9918	0.9826	0.9712	1.0229	1.0154	46.95
0.550	32.935	32.934	0.9910	0.9811	0.9761	1.0193	1.0194	47.40
0.600	35.687	35.686	0.9903	0.9795	0.9803	1.0159	1.0240	46.91
0.650	38.432	38.431	0.9895	0.9780	0.9839	1.0127	1.0293	45.42
0.700	41.173	41.172	0.9888	0.9765	0.9870	1.0098	1.0355	42.87
0.750	43.913	43.912	0.9880	0.9749	0.9897	1.0072	1.0427	39.19
0.800	46.654	46.653	0.9873	0.9734	0.9922	1.0048	1.0512	34.29
0.850	49.400	49.400	0.9865	0.9718	0.9944	1.0028	1.0613	28.02
0.900	52.161	52.161	0.9858	0.9703	0.9964	1.0012	1.0734	20.26
0.950	54.945	54.945	0.9850	0.9687	0.9983	1.0002	1.0885	10.87
1.000	57.778	57.778	0.9842	0.9671	1.0000	1.0000	1.0806	0.0

Experimental Data

The experimental *PTx* data measured for the four systems are given in Tables II–V. The "smooth" pressure values reported 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 et al. method (*2*). 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

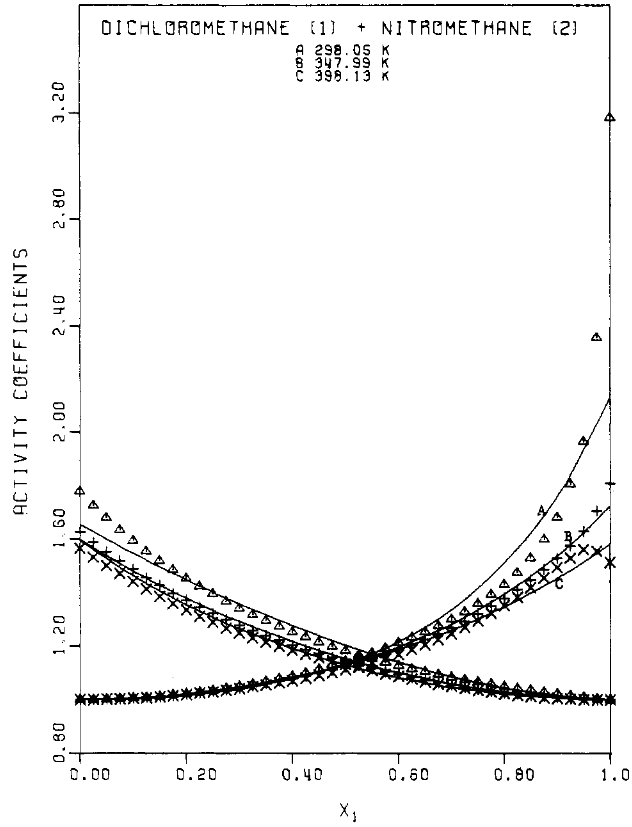

Figure 7. Activity coefficients for the dichloromethane (1) + nitromethane (2) system: curves from Barker results; points from Mixon et al. method.

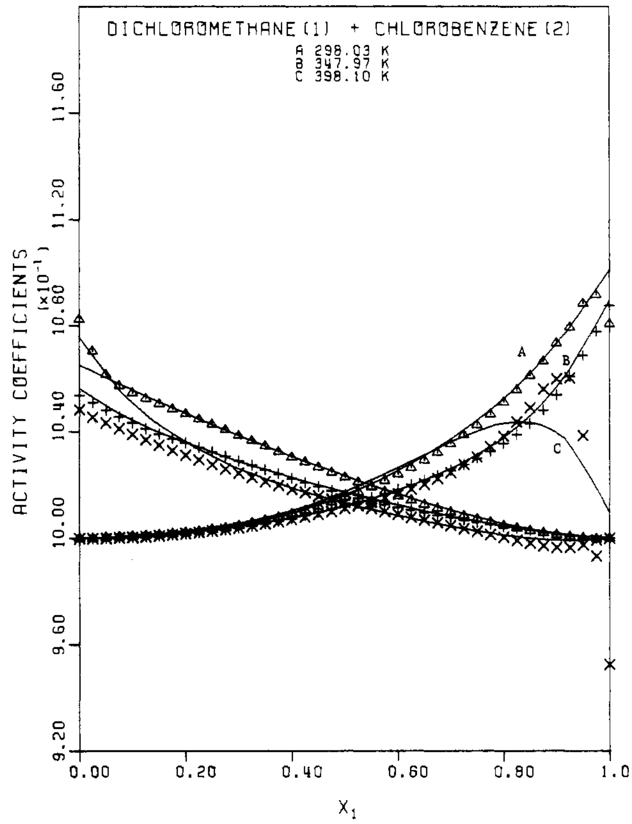

Figure 8. Activity coefficients for the dichloromethane (1) + chlorobenzene (2) system: curves from Barker results; points from Mixon et al. method. The ordinate values run from 0.920 to 1.160.

Table XIV. Calculated Data for the Dichloromethane (1) + Chlorobenzene (2) System at 347.97 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 69.42 COMPONENT 2 = 112.56

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	16.223	16.223	0.9980	0.9928	0.0	1.0539	1.0000	0.0
0.050	30.662	30.661	0.9949	0.9869	0.4939	1.0483	1.0001	7.19
0.100	45.043	45.041	0.9921	0.9813	0.6715	1.0434	1.0005	13.62
0.150	59.398	59.395	0.9894	0.9758	0.7631	1.0393	1.0011	19.35
0.200	73.749	73.747	0.9867	0.9703	0.8192	1.0358	1.0018	24.47
0.250	88.095	88.092	0.9840	0.9649	0.8571	1.0324	1.0027	29.00
0.300	102.425	102.423	0.9814	0.9595	0.8844	1.0291	1.0040	32.91
0.350	116.736	116.733	0.9788	0.9542	0.9051	1.0257	1.0055	36.14
0.400	131.037	131.034	0.9762	0.9488	0.9213	1.0225	1.0075	38.65
0.450	145.346	145.344	0.9735	0.9435	0.9344	1.0194	1.0098	40.40
0.500	159.678	159.677	0.9709	0.9382	0.9453	1.0165	1.0123	41.38
0.550	174.051	174.050	0.9683	0.9329	0.9544	1.0139	1.0152	41.59
0.600	188.480	188.479	0.9657	0.9276	0.9622	1.0116	1.0183	41.01
0.650	202.978	202.977	0.9631	0.9223	0.9690	1.0096	1.0217	39.67
0.700	217.543	217.542	0.9604	0.9169	0.9750	1.0078	1.0255	37.55
0.750	232.167	232.166	0.9578	0.9116	0.9802	1.0061	1.0300	34.61
0.800	246.845	246.844	0.9551	0.9062	0.9850	1.0045	1.0356	30.73
0.850	261.570	261.569	0.9524	0.9008	0.9892	1.0030	1.0432	25.73
0.900	276.348	276.348	0.9498	0.8955	0.9931	1.0015	1.0541	19.25
0.950	291.264	291.264	0.9471	0.8901	0.9966	1.0004	1.0688	10.82
1.000	306.433	306.433	0.9443	0.8846	1.0000	1.0000	1.0877	0.0

Table XV. Calculated Data for the Dichloromethane (1) + Chlorobenzene (2) System at 398.10 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 69.42 COMPONENT 2 = 112.56

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	84.806	84.806	0.9929	0.9736	0.0	1.0485	1.0000	0.0
0.050	128.151	128.146	0.9860	0.9609	0.3620	1.0434	1.0001	7.39
0.100	171.636	171.630	0.9798	0.9489	0.5422	1.0391	1.0005	14.03
0.150	215.303	215.296	0.9739	0.9372	0.6503	1.0350	1.0010	19.92
0.200	259.190	259.182	0.9681	0.9257	0.7226	1.0312	1.0018	25.07
0.250	303.337	303.330	0.9623	0.9142	0.7744	1.0276	1.0028	29.48
0.300	347.784	347.779	0.9566	0.9028	0.8135	1.0244	1.0040	33.16
0.350	392.570	392.567	0.9509	0.8914	0.8442	1.0213	1.0054	36.11
0.400	437.736	437.732	0.9451	0.8800	0.8689	1.0185	1.0071	38.34
0.450	483.317	483.315	0.9394	0.8686	0.8894	1.0159	1.0090	39.83
0.500	529.335	529.333	0.9335	0.8571	0.9066	1.0135	1.0112	40.57
0.550	575.810	575.811	0.9277	0.8456	0.9213	1.0112	1.0137	40.54
0.600	622.762	622.762	0.9218	0.8341	0.9342	1.0090	1.0167	39.70
0.650	670.199	670.200	0.9158	0.8225	0.9454	1.0069	1.0203	37.98
0.700	718.102	718.101	0.9099	0.8109	0.9555	1.0048	1.0247	35.26
0.750	766.438	766.439	0.9038	0.7993	0.9645	1.0026	1.0305	31.37
0.800	815.178	815.177	0.8978	0.7876	0.9726	1.0004	1.0385	26.02
0.850	864.407	864.408	0.8916	0.7759	0.9801	0.9982	1.0493	18.78
0.900	914.704	914.704	0.8854	0.7641	0.9871	0.9966	1.0601	9.24
0.950	968.274	968.274	0.8787	0.7515	0.9939	0.9977	1.0386	-1.01
1.000	1024.766	1024.766	0.8717	0.7383	1.0000	1.0000	0.9524	0.0

the existence of an azeotrope if one exists.

Binaries of dichloromethane with benzene and toluene showed negative deviation from Raoult's law at all temperatures. The dichloromethane + nitromethane system showed a positive deviation at all temperatures. The dichloromethane + chlorobenzene binary was a mixed deviation system at 298 K, showing small positive deviations everywhere except at high dichloromethane concentrations. The deviations were negative for the other two isotherms at all concentrations of dichloromethane. None of the four binary systems exhibited azeotropes at any temperature.

Reduced Data

The calculated y_i, γ_i, and G^E values are reported in Tables VI–XV. Those values were obtained with the Mixon et al. data reduction method, using the Peng–Robinson equation of state (*3*) to estimate the vapor-phase fugacity coefficients. The "experimental" pressure values tabulated in Tables VI–XV 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 (*4*) data reduction methods. The Barker results shown used the five-constant Redlich–Kister G^E equation for the binaries of dichloromethane with benzene, toluene, and chlorobenzene. The Wilson equation results are reported for the dichloromethane

Table XVI. Compound Constants for the Peng-Robinson Equation of State

compd	T_c, K	P_c, MPa	ω
dichloromethane	510.150	6.080	0.1990
benzene	562.160	4.898	0.2092
toluene	594.025	4.236	0.2607
nitromethane	588.000	6.313	0.3460
chlorobenzene	632.350	4.519	0.2490

+ nitromethane system. The points in the figures represent the evenly spaced Mixon et al. values while the curves represent the Barker method results.

The Peng–Robinson equation of state was used for all the results shown. Table XVI lists the compound constants used for the Peng–Robinson equation. The binary interaction constant was set to 0.0 for all four binaries.

Some peculiarities in the tables and figures for the calculated results are worthy of comment. For example, note in Tables VI and VII that the activity coefficient for benzene appears to go through a maximum near the $x_1 = 0$ end. The significant digits for the activity coefficients certainly do not extend to the fourth decimal digit but, nevertheless, it is reasonable to accept as valid a "flatness" in the benzene activity coefficient curve (if not an actual maximum) for this almost ideal system. Note in Tables VIII and IX, and in Figure 6, that toluene behaves in the same manner but without exhibiting a maximum.

The relative sensitivities of the infinite dilution activity coefficients obtained from the Mixon et al. and the Barker methods have been discussed in several preceding papers in this series. The Mixon et al. result is determined by the shape of the P vs. x_1 curve near the end point whereas the Barker result is obtained by the fit of the G^E equation over the entire binary composition range. Sometimes the results differ appreciably, as shown by the right end of the 298.05 K curve in Figure 7. Note in Figure 3 how small the deviation from Raoult's law is at 298.05 K at high x_1 values. The points in Figure 3 appear smooth enough but as discussed in previous papers—for example, (*5*)—errors in the 0.05 mmHg range can have a large effect when the deviation is small. Hence, one would tend to have more confidence in the Barker result in this instance.

A much more obvious example of the effect of scatter on the calculated results is illustrated in the 398.10 K isotherm in Figures 4 and 8. The $x_1 = 0.7891$ point (803.3 kPa) is obviously out of line, and other points on the isotherm show an unusual amount of scatter. As shown by the "smooth" values at 398.10 K in Table V, the cubic splined fit was allowed to fit most of the bad points quite closely. That "overfitted" splined fit has been reported here to illustrate the effect on the Mixon et al. activity coefficient curves when even slightly scattered data are fitted too closely.

The result of the overfitting is shown in Figure 8 where the activity coefficient curves at 398.10 K are obviously wrong for the Mixon et al. method. Anyone who needs the best possible activity coefficient curves for the dichloromethane + chlorobenzene system should first arbitrarily smooth the P vs. x_1 curve and use the smoothed values as input to the data reduction methods. Usually, the Barker method does an effective job of smoothing the P vs. x_1 data but, in this case, a relatively small amount of scatter affects it almost as much as the Mixon et al. method.

Registry No. Dichloromethane, 75-09-2; benzene, 71-43-2; toluene, 108-88-3; nitromethane, 75-52-5; chlorobenzene, 108-90-7.

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Excess Enthalpies of Some Ester + Alcohol Binary Mixtures

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The excess molar enthalpies of the binary liquid mixtures methyl butanoate + normal alcohol (C_4–C_{10}) and propyl ethanoate + normal alcohol (C_3–C_5) have been determined at atmospheric pressure and 298.15 K as a function of mole fraction. The apparatus used was a standard Calvet microcalorimeter equipped with a device allowing the exclusion of a vapor phase. The mixtures studied are all highly endothermic ($H^E > 0$), and the values of the excess molar enthalpies increase with length of the hydrocarbon chain of the alcohol. The H^E–x curves are practically symmetrical, with maxima at mole fractions of alcohol slightly below 0.5.

Introduction

Continuing with the work described in earlier articles (*1*, *2*), we have determined the excess molar enthalpies of the binary liquid mixtures formed by a linear ester (methyl butanoate or propyl ethanoate) and a normal alcohol (ranging from 1-butanol to 1-decanol in the case of methyl butanoate, and from 1-propanol to 1-pentanol in the case of propyl ethanoate), the measurements being made at 298.15 K and over the entire range of concentrations.

Experimental Section

The chemical products used were supplied by Fluka (Buchs, Switzerland). All were better than 99 mol % pure as supplied except the propyl acetate, which was purified before use by washing with saturated aqueous NaCl solution, drying with $MgSO_4$, and triple distillation in a rectifying column, the final purity being 99.6 mol %. Refractive indices and densities were measured with a Zeiss refractometer (Carl Zeiss, Jena, Germany) and a densimeter–vibratometer (Anton Paar, Graz, Austria). The values measured (Table I) agree well with pub-

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