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Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of Diethylamine with Acetone, Acetonitrile, and Methanol

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Total-pressure vapor–liquid equilibrium (VLE) data are reported at 298, 348, and 398 K for each of the three diethylamine binaries with acetone, acetonitrile, and methanol. The experimental *PTx* data were reduced by both the Mixon–Gumowski–Carpenter and Barker methods; the Mixon et al. results were deemed better and are reported. Six G^E correlations were tested in the Barker data reduction method; the results are reported for the correlation for which the best results were obtained. Various equations of state were used to estimate the vapor-phase fugacity coefficients; the Peng–Robinson results were used for the values reported.

Introduction

Total-pressure vapor–liquid equilibrium data for the three systems covered in this paper were measured as part of the continuing effort to expand the accurate vapor–liquid equilibrium data base for a general correlation of mixture properties. The systems were chosen to cover gaps in the UNIFAC parameter table. Data were measured at three temperatures for all the binaries. The apparatus and technique 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 vacuum 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 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

Table I. Chemicals Used

component	vendor	purity, %
diethylamine	Sigma Chemicals	99.9
acetone	Burdick and Jackson	99.9+
acetonitrile	Burdick and Jackson	99.9+
methanol	Fisher Scientific	99.9

Table II. Experimental P vs. x_1 Values for the Diethylamine (1) + Acetone (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	30.67	30.67	0.0	184.84	184.81	0.0	677.1	677.1
0.0381	31.70	31.70	0.0380	189.74	189.81	0.0379	693.1	692.7
0.0567	32.14	32.15	0.0567	191.98	191.99	0.0566	697.7	698.3
0.1325	33.69	33.67	0.1324	199.55	199.37	0.1323	719.5	719.1
0.2094	34.78	34.80	0.2093	204.91	205.12	0.2091	736.4	736.7
0.2951	35.65	35.65	0.2950	209.90	209.79	0.2948	751.3	751.2
0.3987	36.27	36.26	0.3987	213.21	213.21	0.3986	761.7	761.7
0.4793	36.50	36.49	0.4792	214.46	214.44	0.4792	765.2	765.0
0.5966	36.45	36.48	0.5966	214.26	214.31	0.5967	762.4	762.7
0.6964	36.14	36.13	0.6965	212.29	212.28	0.6967	753.9	753.6
0.7878	35.47	35.44	0.7879	208.68	208.61	0.7881	739.0	739.1
0.8549	34.59	34.62	0.8550	204.30	204.36	0.8553	724.3	724.2
0.9164	33.54	33.53	0.9165	198.93	198.95	0.9167	705.9	706.0
0.9564	32.63	32.62	0.9565	194.48	194.44	0.9567	691.1	691.0
1.0000	31.37	31.37	1.0000	188.47	188.48	1.0000	672.2	672.2

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

298.00 K			347.93 K			398.33 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	11.804	11.804	0.0	81.69	81.69	0.0	339.3	339.2
0.0403	15.483	15.485	0.0402	99.95	99.96	0.0400	390.4	390.8
0.0755	18.028	18.023	0.0753	112.96	112.95	0.0750	430.5	430.2
0.1348	21.280	21.286	0.1346	130.28	130.31	0.1342	485.7	485.7
0.2081	24.062	24.057	0.2078	145.96	145.93	0.2074	538.1	538.3
0.2951	26.321	26.329	0.2946	159.43	159.49	0.2939	584.5	584.4
0.3977	28.18	28.17	0.3973	171.09	171.01	0.3968	625.8	625.7
0.4953	29.46	29.47	0.4950	179.15	179.20	0.4945	654.9	654.9
0.5970	30.53	30.53	0.5968	185.61	185.62	0.5964	677.0	677.0
0.6954	31.32	31.32	0.6952	190.25	190.23	0.6950	692.2	692.3
0.7825	31.87	31.87	0.7824	193.18	193.15	0.7824	701.5	701.3
0.8538	32.13	32.14	0.8538	194.25	194.28	0.8539	703.3	703.3
0.9151	32.14	32.14	0.9151	193.78	193.79	0.9152	698.9	699.0
0.9515	31.97	31.97	0.9515	192.40	192.37	0.9516	692.6	692.4
1.0000	31.42	31.42	1.0000	188.59	188.59	1.0000	677.0	677.0

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

297.97 K			348.09 K			398.58 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	16.885	16.889	0.0	150.98	151.26	0.0	746.6	746.5
0.0389	16.404	16.392	0.0389	148.35	148.14	0.0389	736.7	736.8
0.0746	15.955	15.955	0.0746	145.98	145.69	0.0747	730.2	730.1
0.1306	15.278	15.304	0.1306	142.72	142.67	0.1306	722.5	722.5
0.1930	14.686	14.669	0.1930	140.32	140.58	0.1930	716.0	716.0
0.2798	14.407	14.383	0.2798	139.85	140.15	0.2798	710.4	710.5
0.3756	15.390	15.432	0.3755	143.67	143.38	0.3756	710.2	710.0
0.4760	17.744	17.731	0.4758	151.02	150.81	0.4759	712.5	712.7
0.5733	20.579	20.561	0.5731	159.37	159.62	0.5733	715.0	714.8
0.6726	23.511	23.528	0.6724	167.89	167.90	0.6727	714.9	715.0
0.7674	26.060	26.061	0.7673	175.26	175.15	0.7675	712.6	712.6
0.8431	27.91	27.91	0.8430	180.55	180.62	0.8433	707.4	707.4
0.9002	29.25	29.24	0.9001	184.28	184.26	0.9004	701.0	700.9
0.9492	30.35	30.36	0.9492	187.21	187.21	0.9494	692.7	692.8
1.0000	31.48	31.48	1.0000	189.88	189.88	1.0000	681.5	681.5

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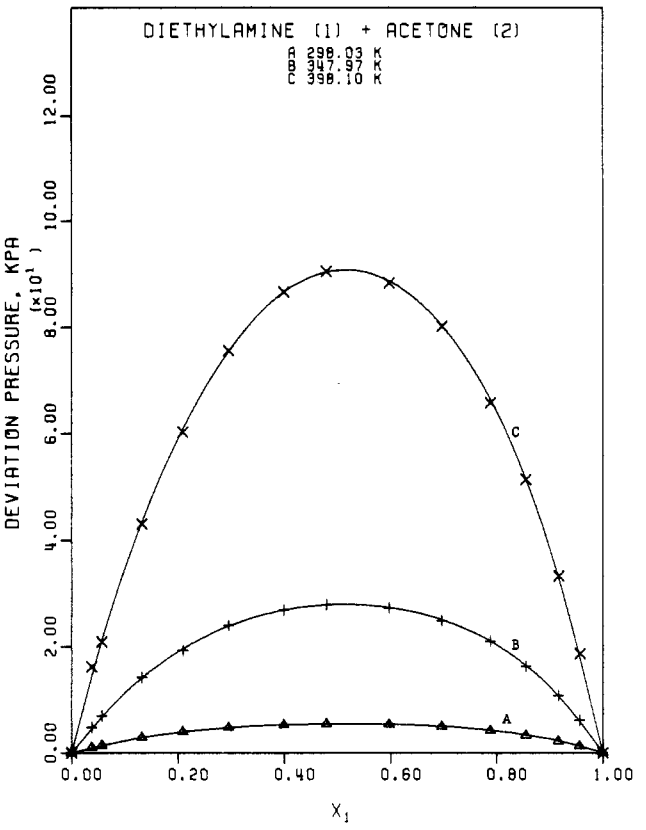

Figure 1. Deviations from Raoult's law for the diethylamine (1) + acetone (2) system. Ordinate values run from 0.0 to 120.0.

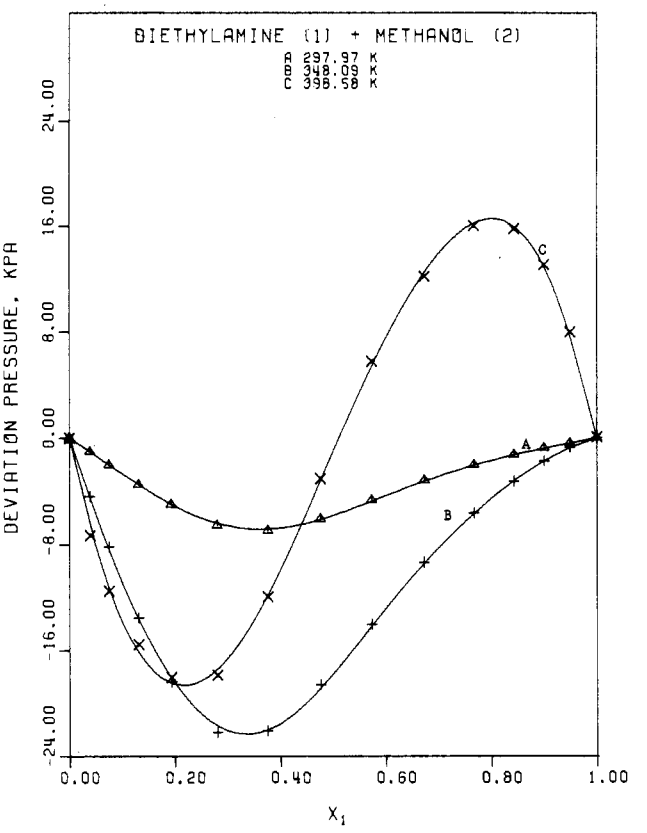

Figure 3. Deviations from Raoult's law for the diethylamine (1) + methanol (2) system.

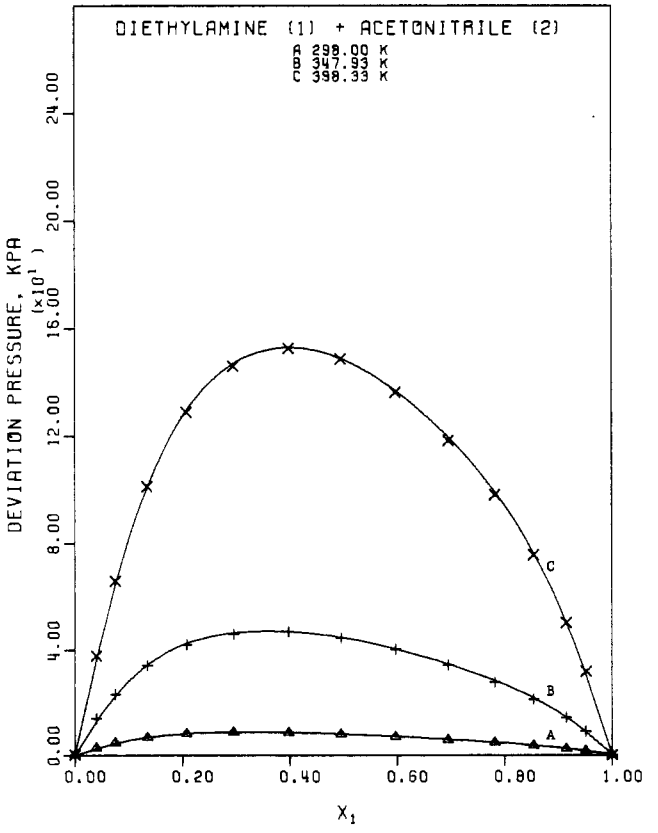

Figure 2. Deviations from Raoult's law for the diethylamine (1) + acetonitrile (2) system. Ordinate values run from 0.0 to 240.0.

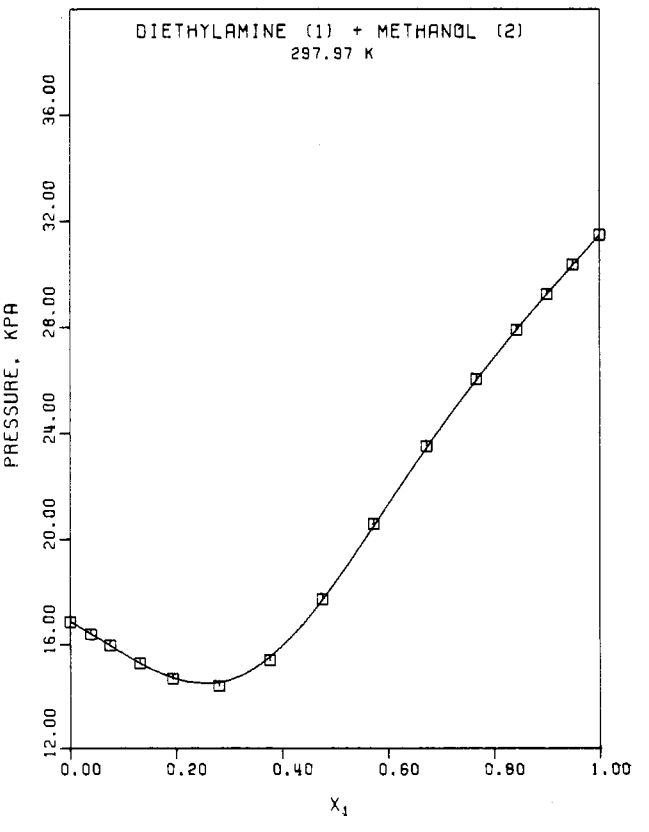

Figure 4. P vs. x_1 plot for the diethylamine (1) + methanol (2) system at 297.97 K.

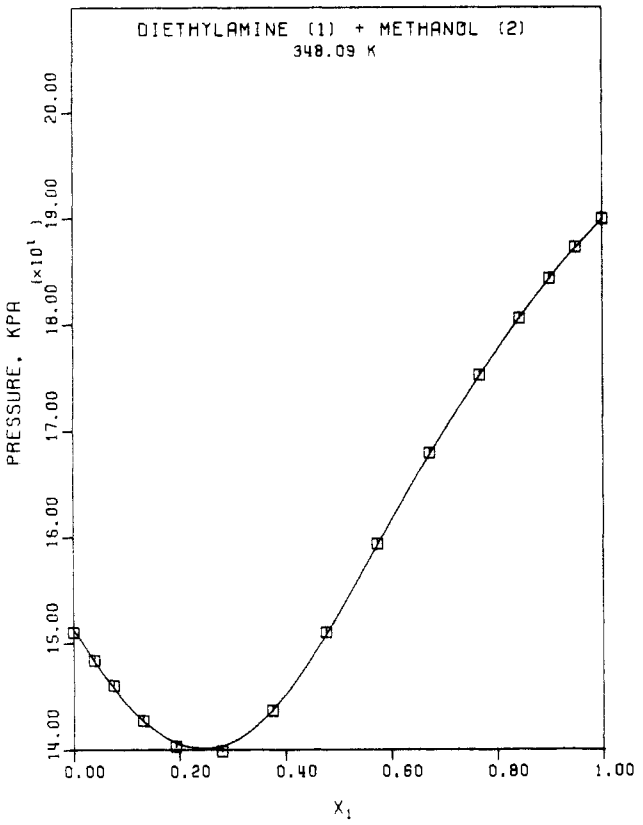

Figure 5. P vs. x_1 plot for the diethylamine (1) + methanol (2) system at 348.09 K. Ordinate values run from 140.0 to 200.0.

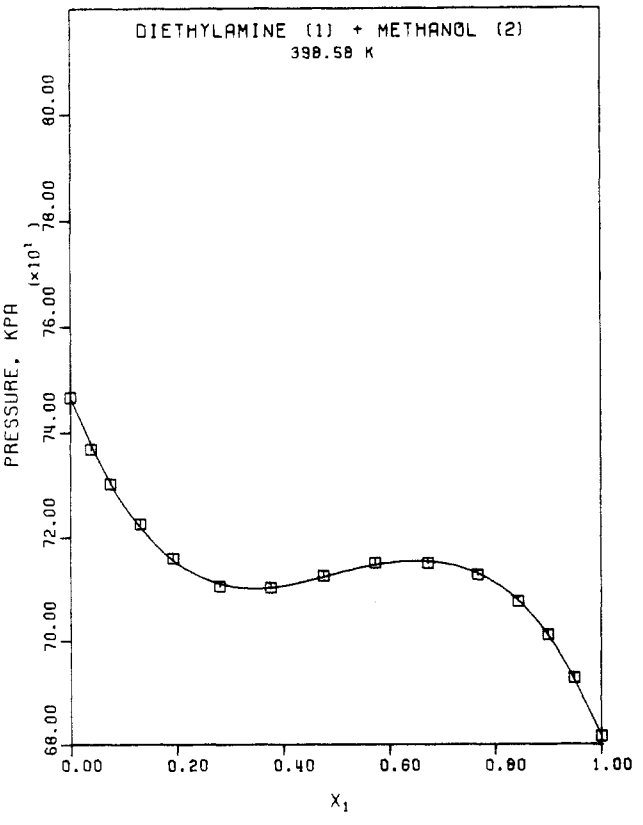

Figure 6. P vs. x_1 plot for the diethylamine (1) + methanol (2) system at 398.58 K. Ordinate values run from 880.0 to 800.0.

Table V. Calculated Data for the Diethylamine (1) + Acetone (2) System at 298.03 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 104.19 COMPONENT 2 = 74.05

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	30.668	30.668	0.9865	0.9885	0.0	1.8979	1.0000	0.0
0.050	31.988	31.988	0.9859	0.9881	0.0872	1.7783	1.0016	75.19
0.100	33.073	33.074	0.9854	0.9877	0.1594	1.6790	1.0063	142.43
0.150	33.963	33.963	0.9850	0.9873	0.2205	1.5897	1.0142	202.02
0.200	34.679	34.680	0.9847	0.9871	0.2732	1.5077	1.0257	253.75
0.250	35.247	35.247	0.9844	0.9868	0.3195	1.4333	1.0409	297.44
0.300	35.688	35.689	0.9842	0.9867	0.3613	1.3672	1.0596	333.02
0.350	36.024	36.025	0.9841	0.9866	0.4001	1.3098	1.0818	360.64
0.400	36.266	36.267	0.9840	0.9865	0.4369	1.2597	1.1074	380.45
0.450	36.426	36.427	0.9839	0.9864	0.4728	1.2171	1.1359	392.65
0.500	36.513	36.514	0.9838	0.9864	0.5096	1.1832	1.1651	397.77
0.550	36.531	36.531	0.9838	0.9864	0.5463	1.1537	1.1982	396.49
0.600	36.473	36.473	0.9839	0.9864	0.5819	1.1248	1.2402	388.18
0.650	36.333	36.333	0.9839	0.9865	0.6178	1.0982	1.2907	372.18
0.700	36.106	36.106	0.9840	0.9866	0.6547	1.0739	1.3521	348.01
0.750	35.778	35.777	0.9841	0.9867	0.6931	1.0517	1.4292	314.84
0.800	35.318	35.317	0.9844	0.9869	0.7355	1.0330	1.5203	271.92
0.850	34.689	34.688	0.9846	0.9871	0.7843	1.0187	1.6237	219.08
0.900	33.857	33.856	0.9850	0.9874	0.8422	1.0086	1.7405	156.42
0.950	32.781	32.780	0.9855	0.9878	0.9119	1.0023	1.8823	83.73
1.000	31.371	31.371	0.9861	0.9884	1.0000	1.0000	2.0586	0.0

Table VI. Calculated Data for the Diethylamine (1) + Acetone (2) System at 347.97 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 113.02 COMPONENT 2 = 80.15

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	184.814	184.814	0.9468	0.9547	0.0	1.6979	1.0000	0.0
0.050	191.230	191.232	0.9449	0.9531	0.0788	1.5980	1.0015	72.05
0.100	196.467	196.470	0.9433	0.9519	0.1456	1.5139	1.0059	135.31
0.150	200.828	200.832	0.9420	0.9508	0.2046	1.4474	1.0123	190.59
0.200	204.513	204.518	0.9409	0.9499	0.2580	1.3927	1.0206	238.92
0.250	207.564	207.569	0.9400	0.9492	0.3067	1.3426	1.0316	280.48
0.300	210.011	210.017	0.9393	0.9486	0.3512	1.2952	1.0457	315.07
0.350	211.889	211.894	0.9387	0.9482	0.3925	1.2507	1.0635	342.30
0.400	213.244	213.249	0.9383	0.9479	0.4313	1.2099	1.0849	361.92
0.450	214.127	214.132	0.9380	0.9477	0.4691	1.1741	1.1092	373.87
0.500	214.586	214.590	0.9379	0.9476	0.5073	1.1449	1.1347	378.55
0.550	214.639	214.644	0.9378	0.9476	0.5456	1.1196	1.1631	376.48
0.600	214.270	214.274	0.9379	0.9477	0.5839	1.0967	1.1962	367.47
0.650	213.456	213.460	0.9381	0.9479	0.6231	1.0764	1.2339	351.33
0.700	212.178	212.181	0.9385	0.9483	0.6634	1.0583	1.2783	327.89
0.750	210.389	210.390	0.9390	0.9487	0.7050	1.0414	1.3339	296.44
0.800	207.958	207.959	0.9397	0.9493	0.7495	1.0268	1.4004	256.14
0.850	204.739	204.740	0.9406	0.9502	0.7989	1.0153	1.4772	206.61
0.900	200.573	200.572	0.9418	0.9512	0.8551	1.0068	1.5664	147.56
0.950	195.235	195.234	0.9433	0.9526	0.9208	1.0017	1.6683	78.70
1.000	188.482	188.482	0.9453	0.9543	1.0000	1.0000	1.7823	0.0

Table VII. Calculated Data for the Diethylamine (1) + Acetone (2) System at 398.10 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 125.48 COMPONENT 2 = 88.28

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	677.064	677.064	0.8683	0.8873	0.0	1.7297	1.0000	0.0
0.050	696.308	696.304	0.8644	0.8842	0.0688	1.4192	1.0039	70.20
0.100	710.599	710.592	0.8615	0.8818	0.1307	1.3690	1.0066	123.51
0.150	723.522	723.511	0.8589	0.8797	0.1887	1.3372	1.0100	172.21
0.200	734.822	734.808	0.8566	0.8779	0.2423	1.3038	1.0155	216.22
0.250	744.275	744.261	0.8547	0.8764	0.2915	1.2678	1.0238	254.69
0.300	751.870	751.855	0.8531	0.8752	0.3372	1.2320	1.0350	286.86
0.350	757.687	757.673	0.8519	0.8743	0.3803	1.1981	1.0490	312.31
0.400	761.804	761.790	0.8511	0.8736	0.4214	1.1668	1.0658	330.81
0.450	764.302	764.287	0.8505	0.8733	0.4615	1.1386	1.0852	342.26
0.500	765.257	765.243	0.8503	0.8732	0.5013	1.1143	1.1067	346.78
0.550	764.686	764.673	0.8503	0.8733	0.5410	1.0924	1.1312	344.48
0.600	762.532	762.518	0.8507	0.8738	0.5810	1.0729	1.1591	335.18
0.650	758.731	758.719	0.8514	0.8745	0.6222	1.0563	1.1895	318.94
0.700	753.220	753.208	0.8524	0.8754	0.6652	1.0425	1.2224	295.92
0.750	745.935	745.925	0.8538	0.8767	0.7104	1.0311	1.2585	266.27
0.800	736.811	736.802	0.8555	0.8783	0.7580	1.0212	1.3013	229.85
0.850	725.563	725.557	0.8577	0.8803	0.8083	1.0122	1.3568	185.70
0.900	711.460	711.455	0.8604	0.8827	0.8636	1.0052	1.4244	132.68
0.950	693.717	693.716	0.8638	0.8857	0.9266	1.0010	1.4998	70.29
1.000	672.168	672.168	0.8680	0.8894	1.0000	1.0000	1.5519	0.0

purity of each chemical was verified chromatographically. Chemicals were handled in a nitrogen atmosphere to prevent contact with water vapor and oxygen. None of the compounds 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 cell at the end of the last isotherm.

Table VIII. Calculated Data for the Diethylamine (1) + Acetonitrile (2) System at 298.00 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 104.18 COMPONENT 2 = 52.80

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	11.804	11.804	0.9948	0.9947	0.0	3.7404	1.0000	0.0
0.050	16.236	16.235	0.9928	0.9927	0.3050	3.1756	1.0040	152.62
0.100	19.511	19.511	0.9913	0.9913	0.4454	2.7820	1.0148	286.30
0.150	21.956	21.956	0.9903	0.9902	0.5258	2.4606	1.0328	402.53
0.200	23.799	23.799	0.9894	0.9894	0.5779	2.1967	1.0579	501.49
0.250	25.256	25.257	0.9888	0.9887	0.6157	1.9858	1.0893	583.83
0.300	26.434	26.434	0.9883	0.9882	0.6452	1.8137	1.1273	650.43
0.350	27.394	27.395	0.9878	0.9878	0.6690	1.6699	1.1731	701.72
0.400	28.200	28.201	0.9875	0.9874	0.6895	1.5495	1.2269	738.00
0.450	28.906	28.906	0.9872	0.9871	0.7082	1.4496	1.2888	759.70
0.500	29.527	29.527	0.9869	0.9868	0.7257	1.3653	1.3606	767.19
0.550	30.073	30.073	0.9867	0.9866	0.7426	1.2931	1.4448	760.54
0.600	30.553	30.553	0.9864	0.9863	0.7592	1.2309	1.5445	739.65
0.650	30.977	30.977	0.9863	0.9862	0.7762	1.1775	1.6629	704.24
0.700	31.355	31.354	0.9861	0.9860	0.7945	1.1326	1.8028	654.07
0.750	31.687	31.686	0.9859	0.9858	0.8151	1.0958	1.9671	589.08
0.800	31.953	31.952	0.9858	0.9857	0.8382	1.0651	2.1697	508.92
0.850	32.127	32.127	0.9858	0.9856	0.8647	1.0398	2.4310	412.38
0.900	32.171	32.170	0.9857	0.9856	0.8955	1.0184	2.8200	297.54
0.950	31.978	31.978	0.9858	0.9857	0.9377	1.0042	3.3458	159.57
1.000	31.420	31.420	0.9861	0.9860	1.0000	1.0000	3.9369	0.0

Table IX. Calculated Data for the Diethylamine (1) + Acetonitrile (2) System at 347.93 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 113.01 COMPONENT 2 = 56.40

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	81.689	81.689	0.9762	0.9758	0.0	3.2089	1.0000	0.0
0.050	103.827	103.827	0.9698	0.9693	0.2445	2.7709	1.0036	157.33
0.100	120.821	120.823	0.9648	0.9643	0.3756	2.4629	1.0132	294.87
0.150	134.050	134.053	0.9610	0.9604	0.4579	2.2109	1.0289	414.38
0.200	144.492	144.496	0.9580	0.9573	0.5150	2.0031	1.0506	516.27
0.250	153.056	153.060	0.9555	0.9548	0.5585	1.8355	1.0776	601.33
0.300	160.194	160.198	0.9534	0.9527	0.5935	1.6969	1.1101	670.49
0.350	166.174	166.178	0.9517	0.9509	0.6226	1.5796	1.1491	724.16
0.400	171.267	171.270	0.9502	0.9494	0.6479	1.4798	1.1949	762.60
0.450	175.701	175.703	0.9490	0.9481	0.6709	1.3953	1.2480	786.10
0.500	179.563	179.564	0.9478	0.9470	0.6924	1.3226	1.3099	794.87
0.550	182.909	182.910	0.9469	0.9460	0.7128	1.2593	1.3828	788.84
0.600	185.796	185.796	0.9460	0.9452	0.7327	1.2042	1.4693	767.72
0.650	188.281	188.281	0.9453	0.9444	0.7529	1.1565	1.5717	731.19
0.700	190.420	190.421	0.9447	0.9438	0.7745	1.1165	1.6909	678.96
0.750	192.223	192.223	0.9442	0.9433	0.7987	1.0841	1.8272	611.20
0.800	193.557	193.556	0.9438	0.9429	0.8256	1.0573	1.9923	527.79
0.850	194.260	194.259	0.9436	0.9427	0.8559	1.0351	2.2024	427.53
0.900	194.096	194.096	0.9436	0.9427	0.8904	1.0162	2.5111	308.26
0.950	192.452	192.451	0.9441	0.9432	0.9358	1.0039	2.9181	165.48
1.000	188.592	188.592	0.9452	0.9443	1.0000	1.0000	3.3855	0.0

Table X. Calculated Data for the Diethylamine (1) + Acetonitrile (2) System at 398.33 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 125.53 COMPONENT 2 = 61.09

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	339.186	339.186	0.9330	0.9313	0.0	2.6023	1.0000	0.0
0.050	402.621	402.622	0.9206	0.9185	0.1856	2.3683	1.0024	150.39
0.100	455.167	455.166	0.9104	0.9080	0.3038	2.1623	1.0099	284.66
0.150	498.325	498.320	0.9020	0.8993	0.3855	1.9808	1.0226	402.47
0.200	533.641	533.632	0.8951	0.8922	0.4456	1.8222	1.0409	503.58
0.250	562.734	562.721	0.8895	0.8864	0.4922	1.6856	1.0647	587.95
0.300	587.236	587.222	0.8847	0.8815	0.5307	1.5705	1.0936	655.88
0.350	608.459	608.443	0.8806	0.8772	0.5643	1.4749	1.1271	708.04
0.400	626.844	626.829	0.8770	0.8735	0.5942	1.3934	1.1662	745.02
0.450	642.678	642.664	0.8739	0.8704	0.6214	1.3227	1.2120	767.00
0.500	656.252	656.239	0.8713	0.8676	0.6468	1.2608	1.2657	773.93
0.550	667.837	667.824	0.8691	0.8653	0.6712	1.2067	1.3286	765.65
0.600	677.665	677.652	0.8672	0.8633	0.6954	1.1598	1.4017	742.00
0.650	685.958	685.946	0.8655	0.8617	0.7205	1.1204	1.4848	702.94
0.700	692.938	692.927	0.8642	0.8603	0.7482	1.0894	1.5736	648.97
0.750	698.614	698.604	0.8631	0.8591	0.7796	1.0666	1.6638	581.61
0.800	702.350	702.342	0.8624	0.8584	0.8130	1.0472	1.7729	501.53
0.850	703.395	703.390	0.8622	0.8582	0.8475	1.0288	1.9292	406.32
0.900	700.813	700.811	0.8627	0.8587	0.8864	1.0131	2.1505	292.34
0.950	692.746	692.745	0.8642	0.8603	0.9353	1.0032	2.4267	156.82
1.000	677.044	677.044	0.8673	0.8635	1.0000	1.0000	2.7457	0.0

Table XI. Calculated Data for the Diethylamine (1) + Methanol (2) System at 297.97 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 104.14 COMPONENT 2 = 40.74

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	16.889	16.889	0.9930	0.9957	0.0	0.1501	1.0000	0.0
0.050	16.255	16.255	0.9932	0.9959	0.0201	0.2094	0.9929	-210.49
0.100	15.655	15.655	0.9935	0.9960	0.0497	0.2490	0.9791	-391.56
0.150	15.088	15.089	0.9937	0.9962	0.0917	0.2954	0.9551	-549.79
0.200	14.612	14.613	0.9938	0.9963	0.1535	0.3592	0.9161	-680.96
0.250	14.364	14.364	0.9939	0.9964	0.2388	0.4396	0.8638	-781.06
0.300	14.483	14.484	0.9938	0.9964	0.3461	0.5352	0.8017	-847.83
0.350	15.019	15.020	0.9935	0.9963	0.4583	0.6298	0.7416	-882.33
0.400	15.901	15.902	0.9930	0.9961	0.5623	0.7155	0.6872	-889.44
0.450	17.052	17.053	0.9925	0.9959	0.6523	0.7908	0.6384	-873.25
0.500	18.395	18.395	0.9919	0.9956	0.7268	0.8548	0.5951	-837.19
0.550	19.858	19.858	0.9912	0.9953	0.7866	0.9072	0.5574	-784.26
0.600	21.372	21.372	0.9905	0.9950	0.8338	0.9481	0.5253	-717.19
0.650	22.873	22.872	0.9899	0.9947	0.8707	0.9774	0.4996	-638.67
0.700	24.294	24.294	0.9892	0.9944	0.8994	0.9950	0.4816	-551.74
0.750	25.619	25.618	0.9886	0.9941	0.9222	1.0035	0.4712	-459.67
0.800	26.869	26.869	0.9881	0.9938	0.9412	1.0064	0.4667	-365.03
0.850	28.069	28.069	0.9875	0.9936	0.9577	1.0063	0.4671	-269.74
0.900	29.237	29.237	0.9870	0.9934	0.9726	1.0047	0.4723	-175.28
0.950	30.375	30.375	0.9865	0.9931	0.9864	1.0023	0.4873	-83.53
1.000	31.483	31.483	0.9860	0.9929	1.0000	1.0000	0.5501	0.0

Table XII. Calculated Data for the Diethylamine (1) + Methanol (2) System at 348.09 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 112.98 COMPONENT 2 = 43.45

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	151.255	151.255	0.9594	0.9753	0.0	0.3819	1.0000	0.0
0.050	147.341	147.342	0.9602	0.9760	0.0310	0.4900	0.9943	-118.94
0.100	144.190	144.193	0.9608	0.9765	0.0732	0.5662	0.9830	-209.34
0.150	141.868	141.871	0.9612	0.9769	0.1246	0.6325	0.9677	-279.69
0.200	140.436	140.440	0.9613	0.9772	0.1841	0.6938	0.9489	-332.92
0.250	139.959	139.963	0.9611	0.9774	0.2504	0.7523	0.9270	-370.58
0.300	140.500	140.503	0.9606	0.9774	0.3219	0.8087	0.9019	-393.52
0.350	142.121	142.124	0.9599	0.9773	0.3968	0.8637	0.8738	-402.22
0.400	144.878	144.880	0.9588	0.9771	0.4730	0.9171	0.8429	-396.90
0.450	148.615	148.616	0.9575	0.9767	0.5454	0.9628	0.8133	-378.28
0.500	152.961	152.961	0.9561	0.9763	0.6106	0.9968	0.7883	-348.73
0.550	157.534	157.533	0.9547	0.9759	0.6674	1.0184	0.7702	-311.13
0.600	161.965	161.964	0.9533	0.9755	0.7156	1.0275	0.7612	-268.77
0.650	166.115	166.113	0.9520	0.9751	0.7574	1.0280	0.7607	-225.03
0.700	170.052	170.050	0.9508	0.9747	0.7955	1.0248	0.7658	-182.02
0.750	173.852	173.850	0.9497	0.9744	0.8314	1.0207	0.7740	-140.87
0.800	177.575	177.573	0.9486	0.9741	0.8662	1.0170	0.7839	-101.96
0.850	181.088	181.087	0.9475	0.9738	0.8992	1.0120	0.8030	-65.96
0.900	184.253	184.252	0.9466	0.9736	0.9309	1.0057	0.8393	-35.92
0.950	187.258	187.257	0.9457	0.9735	0.9647	1.0024	0.8718	-13.38
1.000	189.881	189.881	0.9449	0.9734	1.0000	1.0000	0.9921	0.0

Table XIII. Calculated Data for the Diethylamine (1) + Methanol (2) System at 398.58 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 125.67 COMPONENT 2 = 47.12

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	746.547	746.547	0.8671	0.9198	0.0	0.7229	1.0000	0.0
0.050	734.500	734.501	0.8683	0.9211	0.0395	0.8524	0.9963	-38.22
0.100	726.345	726.346	0.8687	0.9220	0.0859	0.9158	0.9909	-56.36
0.150	720.276	720.276	0.8687	0.9228	0.1338	0.9440	0.9868	-66.21
0.200	715.356	715.356	0.8686	0.9235	0.1847	0.9701	0.9810	-70.90
0.250	711.813	711.812	0.8682	0.9242	0.2388	0.9982	0.9729	-69.77
0.300	709.947	709.942	0.8675	0.9248	0.2954	1.0258	0.9629	-62.32
0.350	709.699	709.695	0.8666	0.9253	0.3519	1.0460	0.9540	-49.22
0.400	710.549	710.544	0.8656	0.9258	0.4067	1.0577	0.9478	-32.29
0.450	711.945	711.944	0.8646	0.9262	0.4589	1.0616	0.9453	-13.34
0.500	713.345	713.345	0.8637	0.9267	0.5080	1.0586	0.9479	5.61
0.550	714.419	714.423	0.8629	0.9273	0.5555	1.0531	0.9534	23.07
0.600	715.061	715.067	0.8623	0.9280	0.6024	1.0469	0.9610	38.45
0.650	715.175	715.185	0.8618	0.9288	0.6489	1.0406	0.9709	51.35
0.700	714.660	714.671	0.8615	0.9298	0.6950	1.0338	0.9842	61.29
0.750	713.301	713.314	0.8614	0.9309	0.7405	1.0260	1.0043	67.30
0.800	710.784	710.798	0.8616	0.9321	0.7862	1.0180	1.0318	68.08
0.850	706.790	706.802	0.8621	0.9336	0.8336	1.0109	1.0667	62.63
0.900	700.940	700.948	0.8631	0.9354	0.8837	1.0051	1.1109	50.01
0.950	692.686	692.690	0.8645	0.9376	0.9385	1.0013	1.1642	29.29
1.000	681.454	681.454	0.8667	0.9404	1.0000	1.0000	1.2249	0.0

Experimental Data

Tables II–IV present the experimental *PTx* data measured for the three binaries. 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 1–3 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 diethylamine + acetone and diethylamine + acetonitrile

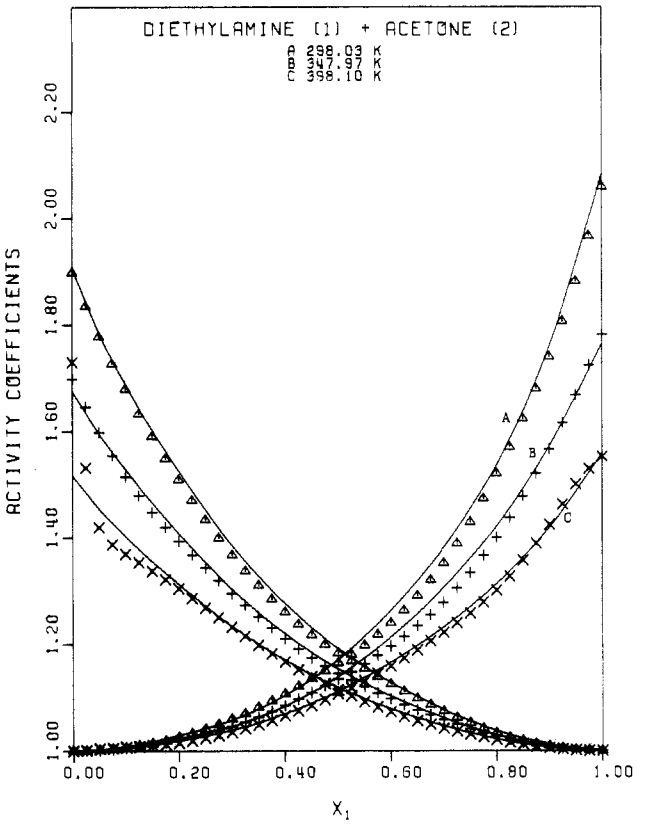

Figure 7. Activity coefficients for the diethylamine (1) + acetone (2) system. Curves from Barker results; points from Mixon et al. method.

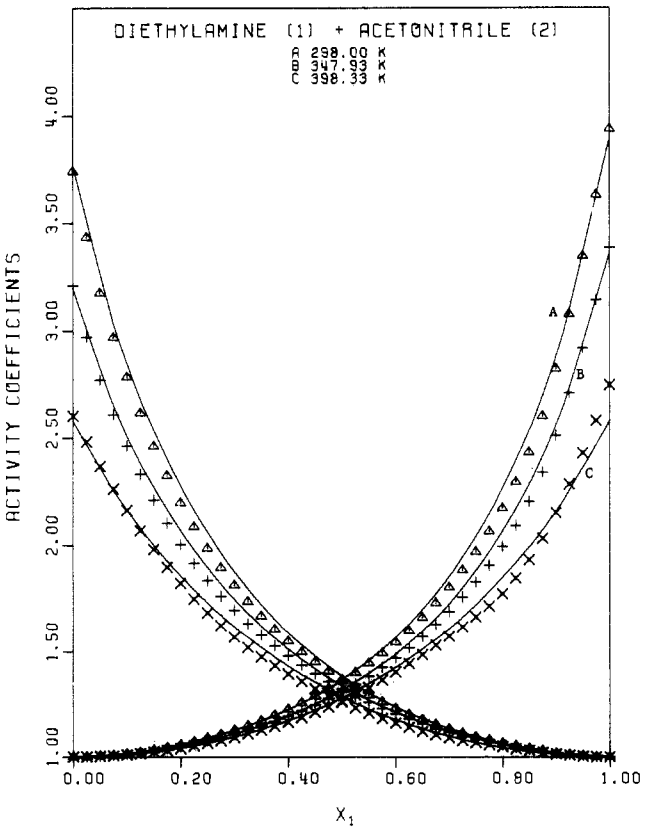

Figure 8. Activity coefficients for the diethylamine (1) + acetonitrile (2) system. Curves from Barker results; points from Mixon et al. method.

binaries exhibited positive deviations from Raoult's law at all three temperatures, and both binaries formed azeotropes at all three temperatures.

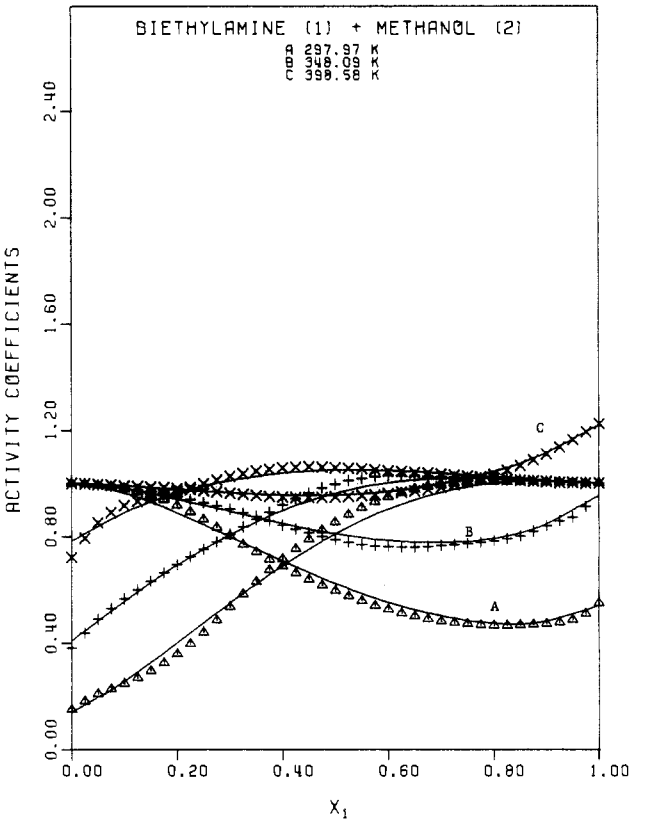

Figure 9. Activity coefficients for the dimethylamine (1) + methanol (2) system. Curves from Barker results; points from Mixon et al. method.

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

compd	T_c, K	P_c, MPa	ω
diethylamine	496.600	3.708	0.2990
acetone	508.100	4.700	0.3073
acetonitrile	548.000	4.833	0.3210
methanol	512.640	8.092	0.5643

The diethylamine + methanol binary showed negative deviations at 298 and 348 K and then became a mixed deviation system at 398 K. As shown by the P vs. x_1 curves in Figures 4–6, maximum-boiling azeotropes were formed at 298 and 348 K, and at 398 K a rare double azeotrope was formed.

Reduced Data

The y_i, γ_i, and G^E values are reported in Tables V–XIII. 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 Table V–XIII 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–IV.) 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 7–9 for both the Mixon et al. (*2*) and the Barker (*4*) data reduction methods. A five-constant Redlich–Kister equation for G^E was used for the Barker calculations for the acetone and methanol binaries. The NRTL equation was found to be better for reducing the data for the diethylamine + acetonitrile system. The points in the plots are the evenly spaced Mixon et al. (*2*) values while the curves represent the Barker (*4*) method re-

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.

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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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