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

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Total pressure vapor–liquid equilibrium (VLE) data are reported at 298, 338, and 388 K for each of the three diethyl ether binaries with acetone, acetonitrile, and methanol. The Mixon–Gumowski–Carpenter and Barker methods were used to reduce the experimental *PTx* data. The Mixon et al. results were found to be better and are reported. The Barker data reduction method was tested for six G^E correlations; the results are shown graphically for the correlation for which the best results were obtained. The Peng–Robinson equation of state was used to estimate the vapor-phase fugacity coefficients.

Introduction

The data for the three systems reported in this paper are part of the continuing effort to expand the vapor–liquid equilibrium data base. This effort was undertaken to fill the existing gaps in the UNIFAC parameter table. The measurements reported in this paper will provide six group interaction parameters with diethyl ether (CH_2O group) as one of the components.

Table I. Chemicals Used

component	vendor	purity, %
diethyl ether	Burdick and Jackson	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 Diethyl Ether (1) + Acetone (2) System

298.06 K			338.19 K			388.30 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	30.68	30.68	0.0	136.23	136.23	0.0	539.9	539.9
0.0320	33.95	33.96	0.0317	146.35	146.35	0.0316	565.5	565.7
0.0716	37.68	37.67	0.0711	157.94	157.94	0.0707	597.3	597.2
0.1341	42.81	42.80	0.1335	174.30	174.29	0.1323	644.0	643.7
0.2040	47.63	47.63	0.2034	190.12	190.14	0.2028	689.2	689.8
0.3042	53.23	53.25	0.3033	208.94	208.90	0.3026	744.2	743.3
0.4016	57.67	57.64	0.4008	223.66	223.70	0.3996	784.6	785.7
0.4984	61.21	61.22	0.4972	235.75	235.75	0.4964	821.9	821.5
0.6007	64.36	64.36	0.6000	246.50	246.46	0.5993	854.8	854.5
0.6984	66.87	66.86	0.6978	254.78	254.81	0.6972	879.8	880.1
0.7927	68.88	68.87	0.7925	261.16	261.18	0.7922	898.6	898.5
0.8610	70.02	70.03	0.8609	264.65	264.62	0.8607	907.6	907.6
0.9150	70.73	70.73	0.9150	266.50	266.51	0.9149	912.0	911.9
0.9538	71.08	71.07	0.9538	267.24	267.24	0.9539	912.4	912.5
1.0000	71.25	71.25	1.0000	267.21	267.21	1.0000	909.5	909.5

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

298.14 K			338.16 K			388.17 X		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	11.837	11.834	0.0	58.63	58.60	0.0	261.75	262.37
0.0430	20.705	20.717	0.0428	87.37	87.45	0.0418	345.1	342.8
0.0815	27.220	27.201	0.0814	109.11	109.04	0.0811	402.7	404.8
0.1409	35.07	35.09	0.1404	135.74	135.70	0.1395	479.7	479.9
0.2068	41.72	41.71	0.2066	158.90	159.00	0.2053	551.6	550.5
0.3006	48.47	48.47	0.2997	183.50	183.41	0.2986	631.4	631.6
0.3962	53.43	53.44	0.3949	201.91	202.00	0.3935	694.5	695.5
0.4981	57.49	57.47	0.4972	217.65	217.54	0.4958	750.1	748.4
0.5965	60.70	60.71	0.5955	230.02	230.14	0.5945	787.0	788.7
0.6971	63.66	63.66	0.6964	241.52	241.46	0.6954	826.0	825.1
0.7857	66.11	66.10	0.7851	250.42	250.43	0.7845	856.8	856.5
0.8511	67.87	67.87	0.8508	256.59	256.60	0.8504	876.9	877.4
0.9142	69.54	69.55	0.9140	262.05	262.08	0.9139	893.0	893.3
0.9502	70.45	70.44	0.9501	264.76	264.73	0.9500	899.9	899.5
1.0000	71.50	71.50	1.0000	267.43	267.43	1.0000	903.4	903.5

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

298.16 K			338.17 K			388.15 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	16.977	16.975	0.0	103.52	103.53	0.0	554.1	553.7
0.0381	24.862	24.871	0.0378	129.55	129.55	0.0376	625.5	626.7
0.0735	31.07	31.06	0.0732	149.97	149.94	0.0730	684.8	684.0
0.1293	38.97	38.97	0.1289	175.76	175.82	0.1284	756.8	755.7
0.1919	45.70	45.71	0.1915	197.84	197.83	0.1910	815.4	816.9
0.2772	52.35	52.31	0.2764	219.54	219.43	0.2750	876.4	876.2
0.3752	57.64	57.69	0.3744	237.01	237.19	0.3736	927.3	927.0
0.4723	61.56	61.52	0.4715	250.01	249.89	0.4710	962.7	962.1
0.5719	64.54	64.55	0.5713	259.69	259.71	0.5781	984.7	986.5
0.6690	66.93	66.93	0.6686	266.92	266.95	0.6689	998.2	996.5
0.7578	68.81	68.80	0.7576	271.83	271.80	0.7582	995.9	996.8
0.8350	70.22	70.22	0.8351	274.20	274.19	0.8358	986.6	986.4
0.8946	71.13	71.13	0.8947	274.29	274.34	0.8955	969.1	969.0
0.9418	71.58	71.57	0.9420	272.63	272.59	0.9426	946.7	946.9
1.0000	71.53	71.53	1.0000	267.10	267.11	1.0000	906.5	906.5

Table V. Calculated Data for the Diethyl Ether (1) + Acetone (2) System at 298.06 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 104.72 COMPONENT 2 = 74.04

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	30.677	30.677	0.9884	0.9885	0.0	1.9482	1.0000	0.0
0.050	35.698	35.700	0.9865	0.9867	0.1808	1.8393	1.0015	78.99
0.100	40.109	40.111	0.9848	0.9850	0.3048	1.7391	1.0061	150.59
0.150	43.979	43.982	0.9833	0.9836	0.3956	1.6472	1.0139	214.59
0.200	47.380	47.383	0.9820	0.9823	0.4654	1.5632	1.0252	270.81
0.250	50.378	50.380	0.9809	0.9812	0.5211	1.4872	1.0402	319.10
0.300	53.040	53.042	0.9799	0.9802	0.5674	1.4190	1.0589	359.39
0.350	55.428	55.429	0.9790	0.9793	0.6070	1.3585	1.0813	391.66
0.400	57.577	57.578	0.9782	0.9785	0.6419	1.3044	1.1080	415.91
0.450	59.517	59.518	0.9774	0.9778	0.6731	1.2558	1.1396	432.06
0.500	61.276	61.276	0.9768	0.9771	0.7018	1.2122	1.1766	439.94
0.550	62.880	62.879	0.9762	0.9765	0.7287	1.1734	1.2197	439.42
0.600	64.343	64.342	0.9756	0.9760	0.7544	1.1388	1.2701	430.29
0.650	65.678	65.678	0.9751	0.9755	0.7795	1.1081	1.3293	412.29
0.700	66.899	66.898	0.9747	0.9750	0.8047	1.0814	1.3986	385.12
0.750	68.011	68.010	0.9742	0.9746	0.8306	1.0585	1.4798	348.48
0.800	69.004	69.003	0.9739	0.9743	0.8575	1.0390	1.5778	301.93
0.850	69.859	69.858	0.9735	0.9739	0.8863	1.0229	1.6991	244.72
0.900	70.557	70.556	0.9733	0.9737	0.9182	1.0106	1.8499	175.96
0.950	71.044	71.043	0.9731	0.9735	0.9552	1.0026	2.0409	94.54
1.000	71.252	71.252	0.9730	0.9734	1.0000	1.0000	2.2569	0.0

Table VI. Calculated Data for the Diethyl Ether (1) + Acetone (2) System at 338.19 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 112.49 COMPONENT 2 = 78.58

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	136.233	136.233	0.9635	0.9639	0.0	1.7685	1.0000	0.0
0.050	151.848	151.853	0.9593	0.9597	0.1426	1.6817	1.0013	76.54
0.100	165.792	165.799	0.9556	0.9560	0.2499	1.6023	1.0052	145.77
0.150	178.257	178.265	0.9523	0.9527	0.3342	1.5298	1.0119	207.60
0.200	189.413	189.421	0.9493	0.9498	0.4027	1.4637	1.0214	261.96
0.250	199.395	199.402	0.9467	0.9472	0.4598	1.4030	1.0341	308.72
0.300	208.336	208.341	0.9443	0.9448	0.5087	1.3475	1.0501	347.72
0.350	216.365	216.369	0.9421	0.9427	0.5514	1.2969	1.0696	378.81
0.400	223.592	223.596	0.9402	0.9408	0.5897	1.2511	1.0929	401.88
0.450	230.124	230.126	0.9385	0.9391	0.6246	1.2098	1.1204	416.79
0.500	236.065	236.067	0.9369	0.9375	0.6573	1.1732	1.1520	423.47
0.550	241.503	241.503	0.9355	0.9361	0.6886	1.1410	1.1880	421.92
0.600	246.460	246.461	0.9342	0.9348	0.7189	1.1126	1.2292	412.10
0.650	250.946	250.947	0.9330	0.9336	0.7487	1.0875	1.2769	393.84
0.700	254.972	254.971	0.9319	0.9325	0.7785	1.0655	1.3324	366.88
0.750	258.535	258.534	0.9309	0.9316	0.8089	1.0465	1.3970	330.90
0.800	261.605	261.604	0.9301	0.9308	0.8405	1.0305	1.4733	285.52
0.850	264.138	264.137	0.9295	0.9301	0.8743	1.0178	1.5623	230.28
0.900	266.074	266.074	0.9289	0.9296	0.9113	1.0086	1.6653	165.04
0.950	267.196	267.195	0.9286	0.9293	0.9522	1.0022	1.8017	88.77
1.000	267.212	267.212	0.9286	0.9293	1.0000	1.0000	1.9663	0.0

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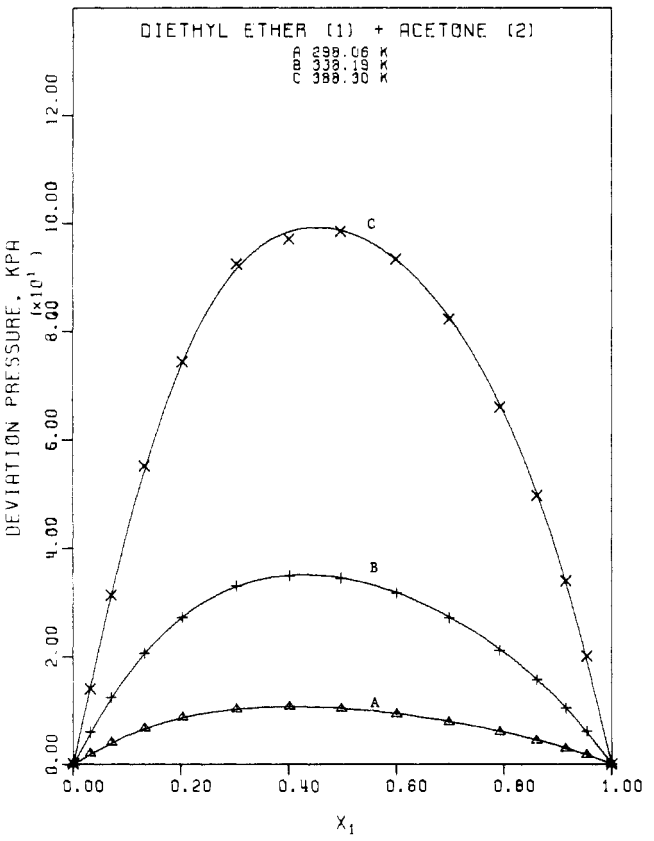

Figure 1. Deviation from Raoult's law for the diethyl ether (1) + acetone (2) system. Ordinate values run from 0.0 to 120.0.

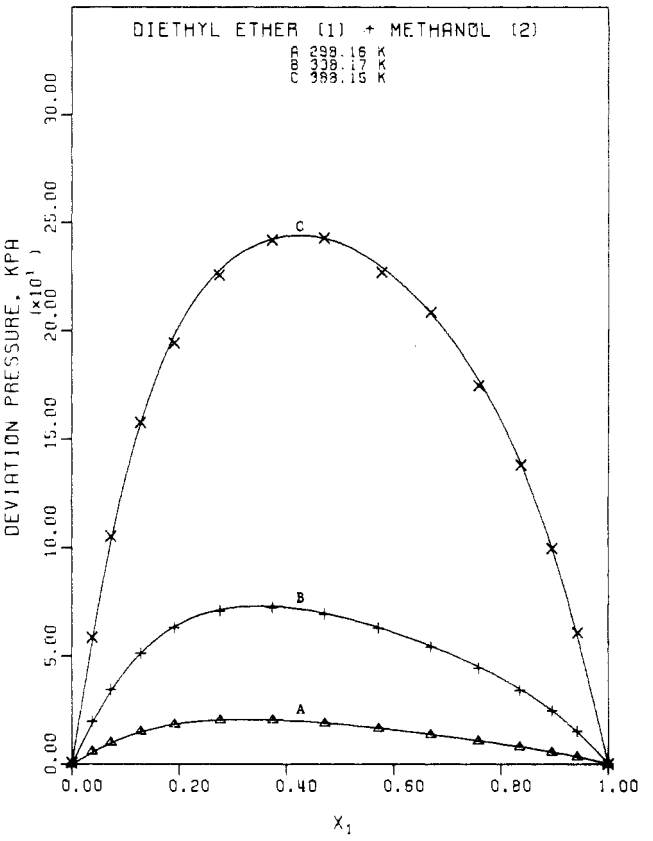

Figure 3. Deviations from Raoult's law for the diethyl ether (1) + methanol (2) system. Ordinate values run from 0.0 to 300.0.

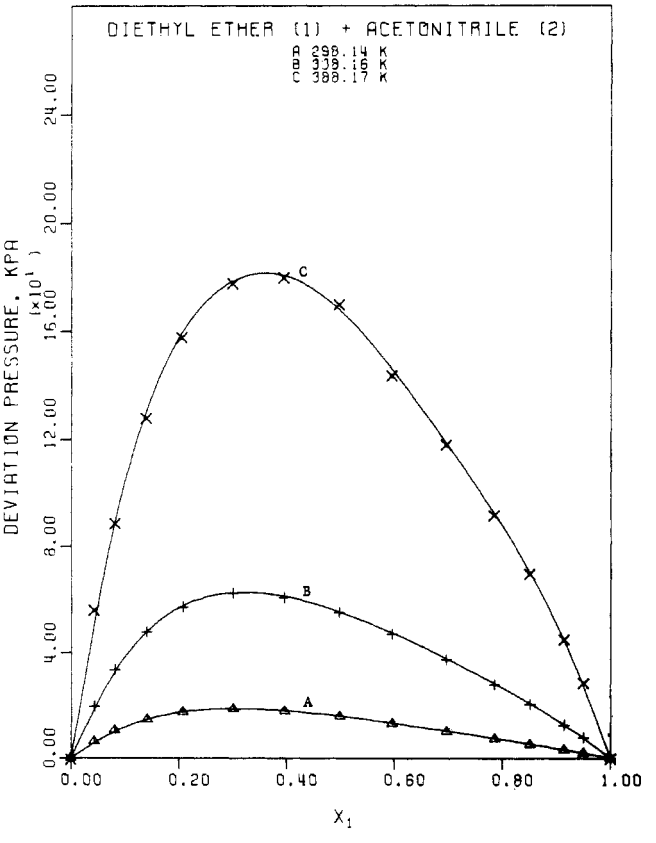

Figure 2. Deviations from Raoult's law for the diethyl ether (1) + acetonitrile (1) system. Ordinate values run from 0.0 to 240.0.

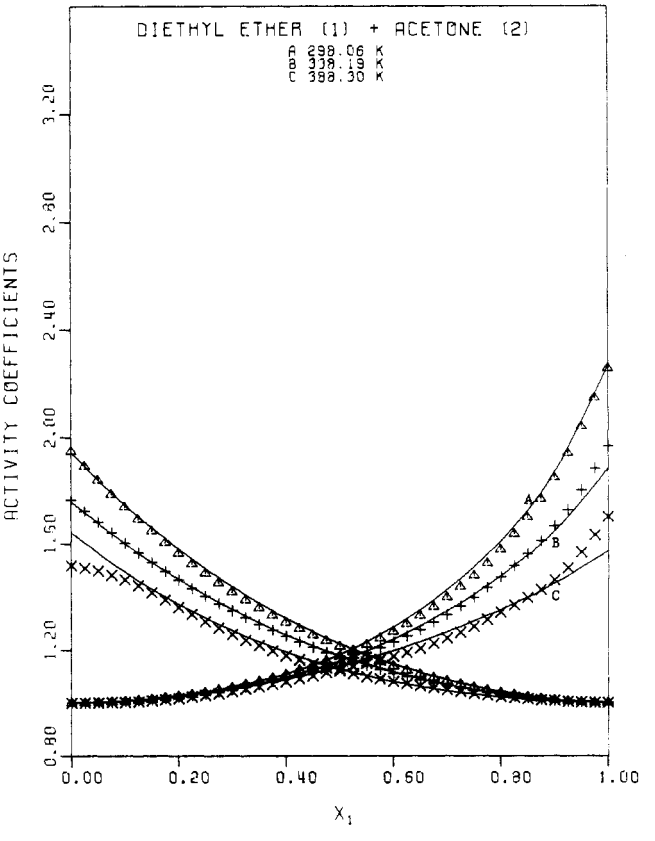

Figure 4. Activity coefficients for the diethyl ether (1) + acetone (2) system. Curves from Barker results; points from Mixon et al. method.

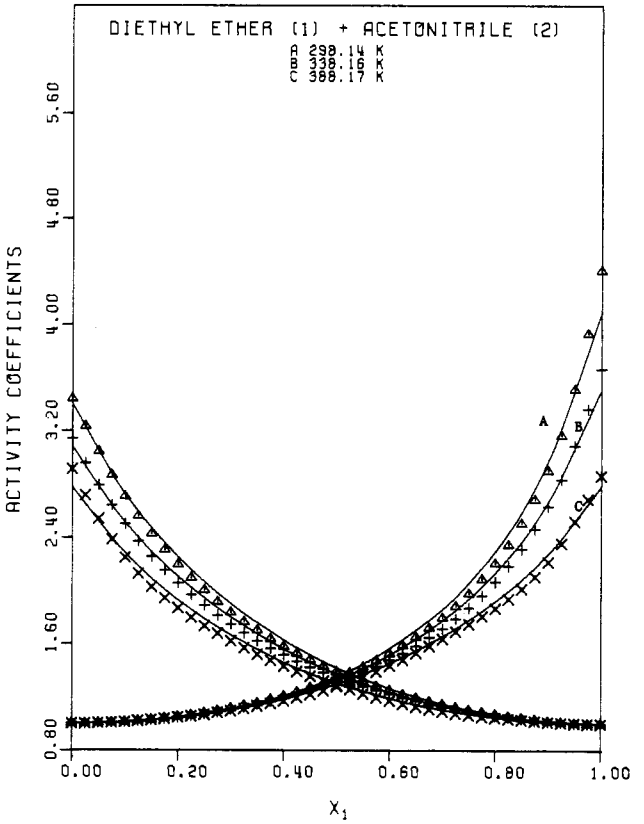

Figure 5. Activity coefficients for the diethyl ether (1) + acetonitrile (2) system. Curves from Barker results; points from Mixon et al. method.

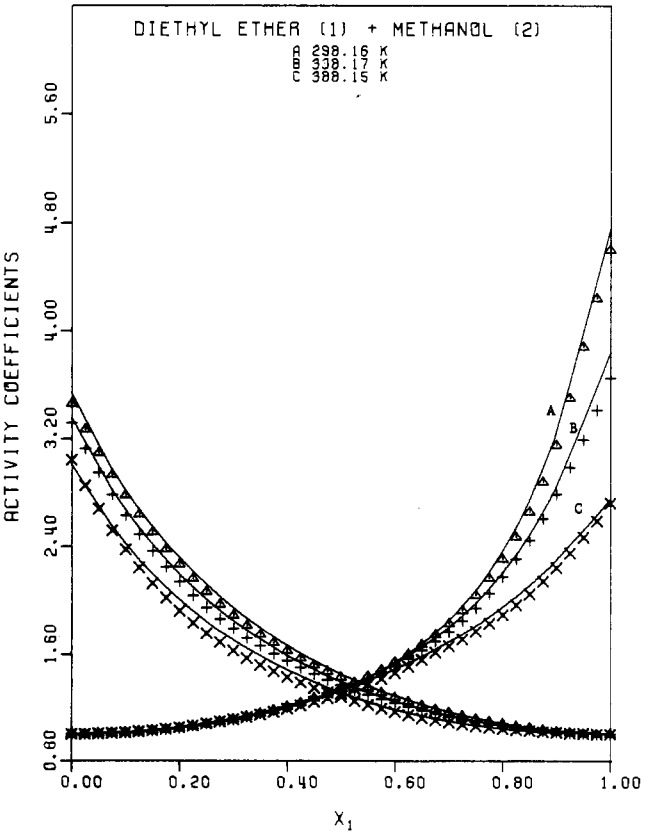

Figure 6. Activity coefficients for the diethyl ether (1) + methanol (2) system. Curves from Barker results; points from Mixon et al. method.

Table VII. Calculated Data for the Diethyl Ether (1) + Acetone (2) System at 388.30 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 126.83 COMPONENT 2 = 85.90

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	539.853	539.853	0.9033	0.9033	0.0	1.5177	1.0000	0.0
0.050	580.649	580.647	0.8961	0.8961	0.1083	1.4978	1.0004	66.36
0.100	619.943	619.939	0.8891	0.8891	0.2002	1.4643	1.0023	129.80
0.150	656.028	656.022	0.8827	0.8827	0.2768	1.4159	1.0072	188.18
0.200	688.076	688.072	0.8771	0.8770	0.3407	1.3604	1.0158	239.35
0.250	716.546	716.539	0.8721	0.8720	0.3955	1.3069	1.0278	282.35
0.300	741.998	741.991	0.8676	0.8675	0.4441	1.2584	1.0426	316.92
0.350	764.963	764.956	0.8635	0.8634	0.4882	1.2156	1.0601	343.12
0.400	785.836	785.829	0.8599	0.8597	0.5292	1.1785	1.0800	361.18
0.450	804.972	804.964	0.8565	0.8563	0.5682	1.1468	1.1020	371.38
0.500	822.725	822.719	0.8534	0.8531	0.6061	1.1204	1.1253	374.17
0.550	839.336	839.331	0.8505	0.8502	0.6436	1.0990	1.1496	370.12
0.600	854.681	854.677	0.8478	0.8475	0.6806	1.0806	1.1761	359.65
0.650	868.562	868.560	0.8453	0.8450	0.7169	1.0641	1.2067	342.71
0.700	880.782	880.780	0.8432	0.8428	0.7527	1.0488	1.2437	318.90
0.750	891.180	891.179	0.8413	0.8410	0.7884	1.0348	1.2888	287.50
0.800	899.714	899.714	0.8398	0.8395	0.8252	1.0229	1.3411	247.93
0.850	906.371	906.371	0.8387	0.8383	0.8642	1.0140	1.3968	200.12
0.900	911.012	911.012	0.8378	0.8375	0.9056	1.0076	1.4619	144.56
0.950	912.551	912.549	0.8376	0.8372	0.9495	1.0021	1.5659	78.91
1.000	909.458	909.458	0.8381	0.8377	1.0000	1.0000	1.7026	0.0

Table VIII. Calculated Data for the Diethyl Ether (1) + Acetonitrile (2) System at 298.14 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 104.72 COMPONENT 2 = 52.65

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	11.834	11.834	0.9955	0.9947	0.0	3.4398	1.0000	0.0
0.050	21.986	21.986	0.9917	0.9902	0.4846	3.0440	1.0031	145.36
0.100	29.897	29.898	0.9887	0.9867	0.6362	2.7079	1.0127	275.11
0.150	36.117	36.118	0.9863	0.9839	0.7102	2.4283	1.0286	389.23
0.200	41.106	41.107	0.9844	0.9817	0.7547	2.1979	1.0505	488.18
0.250	45.132	45.133	0.9829	0.9799	0.7844	2.0031	1.0792	572.24
0.300	48.433	48.434	0.9817	0.9785	0.8060	1.8380	1.1150	641.51
0.350	51.223	51.224	0.9806	0.9772	0.8228	1.6990	1.1580	696.21
0.400	53.614	53.615	0.9797	0.9762	0.8367	1.5805	1.2093	736.56
0.450	55.692	55.692	0.9789	0.9753	0.8484	1.4785	1.2704	762.55
0.500	57.543	57.543	0.9782	0.9744	0.8589	1.3908	1.3428	774.14
0.550	59.241	59.240	0.9776	0.9737	0.8687	1.3156	1.4279	771.25
0.600	60.821	60.821	0.9770	0.9730	0.8782	1.2508	1.5289	753.78
0.650	62.311	62.311	0.9764	0.9723	0.8877	1.1948	1.6503	721.39
0.700	63.737	63.737	0.9759	0.9717	0.8974	1.1466	1.7979	673.58
0.750	65.124	65.123	0.9753	0.9711	0.9077	1.1054	1.9802	609.68
0.800	66.487	66.486	0.9748	0.9705	0.9193	1.0708	2.2100	528.79
0.850	67.840	67.840	0.9743	0.9699	0.9327	1.0427	2.5061	429.73
0.900	69.182	69.182	0.9738	0.9693	0.9490	1.0212	2.9022	311.02
0.950	70.435	70.434	0.9733	0.9688	0.9696	1.0059	3.5151	169.67
1.000	71.501	71.501	0.9729	0.9683	1.0000	1.0000	4.4118	0.0

Table IX. Calculated Data for the Diethyl Ether (1) + Acetonitrile (2) System at 338.16 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 112.51 COMPONENT 2 = 55.68

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	58.603	58.603	0.9844	0.9813	0.0	3.1390	1.0000	0.0
0.050	91.769	91.771	0.9754	0.9707	0.3845	2.7916	1.0030	152.36
0.100	118.187	118.190	0.9684	0.9623	0.5389	2.4987	1.0121	287.81
0.150	139.459	139.463	0.9627	0.9556	0.6228	2.2561	1.0269	406.57
0.200	156.934	156.938	0.9580	0.9501	0.6762	2.0561	1.0473	509.27
0.250	171.379	171.383	0.9541	0.9455	0.7136	1.8868	1.0737	596.30
0.300	183.480	183.482	0.9509	0.9417	0.7416	1.7426	1.1066	667.81
0.350	193.855	193.857	0.9481	0.9385	0.7639	1.6202	1.1461	724.03
0.400	202.860	202.861	0.9457	0.9356	0.7825	1.5153	1.1931	765.17
0.450	210.787	210.787	0.9436	0.9331	0.7986	1.4247	1.2487	791.25
0.500	217.927	217.926	0.9417	0.9309	0.8132	1.3468	1.3139	802.25
0.550	224.525	224.524	0.9400	0.9288	0.8270	1.2801	1.3897	798.22
0.600	230.672	230.670	0.9383	0.9269	0.8403	1.2226	1.4790	779.09
0.650	236.425	236.423	0.9368	0.9251	0.8536	1.1727	1.5853	744.59
0.700	241.842	241.840	0.9354	0.9234	0.8671	1.1296	1.7139	694.19
0.750	246.974	246.972	0.9340	0.9218	0.8814	1.0925	1.8717	627.15
0.800	251.858	251.857	0.9327	0.9203	0.8969	1.0612	2.0690	542.53
0.850	256.525	256.524	0.9315	0.9188	0.9149	1.0361	2.3174	439.14
0.900	260.934	260.933	0.9303	0.9174	0.9365	1.0174	2.6345	315.94
0.950	264.719	264.718	0.9293	0.9163	0.9632	1.0045	3.0906	170.63
1.000	267.434	267.434	0.9286	0.9155	1.0000	1.0000	3.6683	0.0

The apparatus and techniques for the experimental measurements have been described in detail in a previous paper by Maher and Smith (*1*) along with the defining equations for the activity coefficients and the standard states used.

Chemicals used

Table I lists the chemicals used and their stated purities. All chemicals were available in at least 99.9% purity. Activated

Table X. Calculated Data for the Diethyl Ether (1) + Acetonitrile (2) System at 388.17 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 126.34 COMPONENT 2 = 60.48

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	262.367	262.367	0.9530	0.9428	0.0	2.9122	1.0000	0.0
0.050	356.764	356.755	0.9360	0.9224	0.2821	2.5396	1.0035	161.08
0.100	430.910	430.911	0.9228	0.9064	0.4206	2.2474	1.0134	300.03
0.150	491.961	491.959	0.9119	0.8933	0.5060	2.0288	1.0282	418.74
0.200	545.204	545.190	0.9024	0.8819	0.5670	1.8661	1.0465	520.04
0.250	591.867	591.844	0.8941	0.8720	0.6133	1.7337	1.0691	605.65
0.300	632.651	632.623	0.8869	0.8632	0.6498	1.6204	1.0968	676.14
0.350	668.241	668.217	0.8806	0.8556	0.6796	1.5214	1.1307	731.60
0.400	699.281	699.262	0.8751	0.8490	0.7047	1.4337	1.1717	771.87
0.450	726.404	726.390	0.8703	0.8432	0.7264	1.3557	1.2212	796.63
0.500	750.241	750.227	0.8661	0.8381	0.7458	1.2863	1.2806	805.47
0.550	771.452	771.436	0.8624	0.8336	0.7638	1.2252	1.3515	797.96
0.600	790.775	790.749	0.8590	0.8295	0.7814	1.1721	1.4349	773.73
0.650	808.961	808.927	0.8557	0.8257	0.7995	1.1275	1.5308	732.69
0.700	826.765	826.732	0.8526	0.8219	0.8194	1.0918	1.6364	675.21
0.750	844.581	844.558	0.8494	0.8181	0.8419	1.0648	1.7475	602.44
0.800	861.716	861.713	0.8464	0.8145	0.8667	1.0442	1.8695	515.48
0.850	877.271	877.285	0.8436	0.8113	0.8936	1.0276	2.0172	414.26
0.900	890.276	890.300	0.8413	0.8086	0.9228	1.0137	2.2215	297.09
0.950	899.456	899.479	0.8397	0.8067	0.9565	1.0034	2.5234	159.70
1.000	903.460	903.460	0.8390	0.8061	1.0000	1.0000	2.8681	0.0

Table XI. Calculated Data for the Diethyl Ether (1) + Methanol (2) System at 298.16 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 104.73 COMPONENT 2 = 44.89

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	16.975	16.975	0.9938	0.9957	0.0	3.4546	1.0000	0.0
0.050	27.065	27.066	0.9899	0.9932	0.4009	3.0922	1.0029	146.65
0.100	35.077	35.078	0.9868	0.9912	0.5573	2.7759	1.0117	279.04
0.150	41.419	41.420	0.9844	0.9897	0.6400	2.5028	1.0268	396.83
0.200	46.448	46.449	0.9825	0.9885	0.6911	2.2681	1.0485	499.89
0.250	50.458	50.459	0.9809	0.9875	0.7258	2.0666	1.0772	588.09
0.300	53.735	53.736	0.9797	0.9868	0.7515	1.8964	1.1128	661.47
0.350	56.478	56.479	0.9787	0.9861	0.7718	1.7524	1.1559	720.28
0.400	58.782	58.783	0.9778	0.9856	0.7884	1.6286	1.2079	764.61
0.450	60.739	60.740	0.9770	0.9851	0.8025	1.5213	1.2704	794.32
0.500	62.440	62.440	0.9764	0.9847	0.8150	1.4284	1.3449	809.25
0.550	63.943	63.943	0.9758	0.9844	0.8266	1.3478	1.4341	809.18
0.600	65.285	65.285	0.9753	0.9841	0.8376	1.2775	1.5421	793.73
0.650	66.498	66.497	0.9749	0.9838	0.8485	1.2161	1.6741	762.35
0.700	67.615	67.614	0.9744	0.9835	0.8598	1.1629	1.8372	714.31
0.750	68.650	68.649	0.9740	0.9833	0.8720	1.1172	2.0427	648.73
0.800	69.603	69.603	0.9737	0.9831	0.8858	1.0783	2.3087	564.35
0.850	70.474	70.474	0.9733	0.9829	0.9026	1.0467	2.6580	459.60
0.900	71.200	71.200	0.9731	0.9828	0.9238	1.0218	3.1517	332.69
0.950	71.613	71.613	0.9729	0.9828	0.9534	1.0046	3.8790	178.89
1.000	71.535	71.535	0.9729	0.9829	1.0000	1.0000	4.6016	0.0

Table XII. Calculated Data for Diethyl Ether (1) + Methanol (2) System at 338.17 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 112.50 COMPONENT 2 = 47.76

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	103.525	103.525	0.9734	0.9816	0.0	3.3152	1.0000	0.0
0.050	136.966	136.970	0.9641	0.9758	0.2751	2.9442	1.0031	159.96
0.100	163.254	163.261	0.9569	0.9714	0.4156	2.6283	1.0123	302.72
0.150	183.957	183.964	0.9513	0.9679	0.5007	2.3630	1.0278	428.26
0.200	200.379	200.386	0.9469	0.9652	0.5581	2.1401	1.0496	536.84
0.250	213.500	213.507	0.9433	0.9631	0.5996	1.9517	1.0781	628.60
0.300	224.267	224.272	0.9404	0.9613	0.6320	1.7943	1.1130	703.82
0.350	233.312	233.316	0.9380	0.9599	0.6587	1.6627	1.1546	762.99
0.400	240.930	240.933	0.9359	0.9587	0.6814	1.5501	1.2041	806.38
0.450	247.395	247.397	0.9342	0.9577	0.7013	1.4531	1.2631	834.00
0.500	252.977	252.978	0.9327	0.9568	0.7196	1.3696	1.3325	845.79
0.550	257.841	257.841	0.9313	0.9560	0.7369	1.2975	1.4147	841.68
0.600	262.063	262.063	0.9302	0.9554	0.7537	1.2348	1.5129	821.38
0.650	265.717	265.717	0.9292	0.9549	0.7707	1.1803	1.6311	784.43
0.700	268.868	268.868	0.9283	0.9545	0.7887	1.1336	1.7738	730.30
0.750	271.462	271.461	0.9276	0.9541	0.8082	1.0937	1.9499	658.35
0.800	273.357	273.357	0.9271	0.9539	0.8300	1.0597	2.1748	567.38
0.850	274.408	274.408	0.9268	0.9539	0.8572	1.0336	2.4453	456.16
0.900	274.238	274.238	0.9268	0.9542	0.8915	1.0147	2.7853	324.92
0.950	272.076	272.075	0.9274	0.9548	0.9374	1.0035	3.1916	172.39
1.000	267.111	267.111	0.9287	0.9561	1.0000	1.0000	3.6474	0.0

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 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 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 XIII. Calculated Data for the Diethyl Ether (1) + Methanol (2) System at 388.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 126.77 COMPONENT 2 = 52.34

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	553.683	553.683	0.9058	0.9353	0.0	3.0385	1.0000	0.0
0.050	647.991	647.992	0.8882	0.9245	0.1749	2.6755	1.0033	168.80
0.100	721.475	721.469	0.8746	0.9164	0.2839	2.3747	1.0130	316.62
0.150	778.902	778.891	0.8641	0.9101	0.3588	2.1288	1.0289	443.91
0.200	824.247	824.226	0.8558	0.9053	0.4141	1.9276	1.0508	551.45
0.250	860.529	860.503	0.8491	0.9015	0.4574	1.7620	1.0785	639.85
0.300	890.662	890.633	0.8436	0.8984	0.4939	1.6285	1.1111	710.17
0.350	916.303	916.273	0.8389	0.8959	0.5263	1.5201	1.1486	763.54
0.400	937.860	937.835	0.8349	0.8938	0.5553	1.4286	1.1921	800.72
0.450	955.687	955.665	0.8316	0.8921	0.5819	1.3496	1.2433	821.94
0.500	970.131	970.112	0.8289	0.8908	0.6067	1.2806	1.3038	827.15
0.550	981.427	981.412	0.8267	0.8899	0.6304	1.2200	1.3756	816.07
0.600	989.720	989.708	0.8251	0.8893	0.6536	1.1667	1.4614	788.27
0.650	995.151	995.141	0.8240	0.8891	0.6778	1.1211	1.5618	743.30
0.700	997.821	997.816	0.8233	0.8893	0.7064	1.0868	1.6651	681.77
0.750	997.280	997.276	0.8232	0.8899	0.7393	1.0610	1.7743	605.93
0.800	992.679	992.679	0.8238	0.8910	0.7757	1.0398	1.9020	515.73
0.850	983.157	983.156	0.8253	0.8928	0.8170	1.0231	2.0538	410.94
0.900	967.272	967.271	0.8280	0.8955	0.8650	1.0103	2.2433	290.45
0.950	942.569	942.569	0.8322	0.8992	0.9242	1.0025	2.4665	153.44
1.000	906.485	906.485	0.8385	0.9045	1.0000	1.0000	2.7217	0.0

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

compd	T_c, K	P_c, MPa	ω
diethyl ether	466.7	3.637	0.2810
acetone	508.100	4.700	0.3073
acetonitrile	548.000	4.833	0.3210
methanol	512.640	8.092	0.5643

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

	max % dev in P[a]		rms for % dev[b]	
temp, K	Barker	Mixon	Barker	Mixon
	Diethylether(1) + Acetone(2)			
298.06	0.052	0.042	0.023	0.020
338.19	0.399	0.018	0.274	0.009
388.30	0.551	0.133	0.318	0.058
	Diethylether(1) + Acetonitrile(2)			
298.14	0.119	0.072	0.055	0.031
338.16	0.147	0.095	0.093	0.044
388.17	0.515	0.648	0.218	0.248
	Diethylether(1) + Methanol(2)			
298.16	0.072	0.083	0.032	0.035
338.17	0.049	0.073	0.028	0.029
388.15	0.454	0.198	0.190	0.110

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

Experimental Data

The experimental *PTx* data measured for the three binaries is presented in Tables II–IV. 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

Table XVI. Effect of the Calculation Method on γ_i^∞ for the Diethyl Ether (1) + Methanol (2) System. Peng-Robinson Equation of State Used

Calculation method	Accuracy of P fits, max % dev/rmsd			Calculated γ_i^∞ values					
				Component 1			Component 2		
	298.16K	338.17K	388.15K	298.16K	338.17K	388.15K	298.16K	338.17K	388.15K
Mixon et al.	0.0/0.0	0.0/0.0	0.1/0.1	3.455	3.315	3.038	4.602	3.647	2.722
Barker:									
absolute Van Laar	1.3/0.6	0.7/0.4	0.4/0.2	3.291	3.174	2.967	4.323	3.600	2.738
Wilson	0.3/0.2	0.2/0.1	0.2/0.1	3.463	3.307	3.056	4.707	3.795	2.806
NRTL	0.4/0.2	0.1/0.0	0.3/0.1	3.538	3.353	3.004	4.766	3.839	2.748
modified Margules	0.2/0.0	0.1/0.0	1.9/1.0	3.491	3.353	3.626	4.901	3.829	3.493
UNIQUAC	1.1/0.6	0.6/0.3	0.3/0.1	3.302	3.187	2.984	4.402	3.642	2.755
Redlich-Kister, three constant	0.6/0.2	0.8/0.5	0.3/0.1	3.570	3.350	2.997	4.650	3.455	2.760
Redlich-Kister, five constant	0.0/0.0	0.0/0.0	0.4/0.2	3.450	3.303	2.961	4.830	3.771	2.730
Gautreaux-Coates:									
splined fits				3.453	3.314	3.038	4.588	3.643	2.720
P_D/x_1x_2 plots				3.413	3.286	2.979	4.518	3.589	2.672

are the pure component vapor pressures.

All the three binaries exhibited positive deviations from Raoult's law at all the three temperatures. The diethyl ether + acetonitrile system did not form any azeotropes. The diethyl ether + acetone system formed azeotropes at 338 and 388 K. The diethyl ether + methanol system formed azeotropes at all the three temperatures studied.

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 Tables V–XIII are actually interpolated values from the cubic splined fits of the experimental P vs. x_1 values. 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 4–6 for both the Mixon et al. and the Barker (*4*) data reduction methods. A five-constant Redlich–Kister equation for G^E was used for the Barker calculations for all the three binaries. The points in the plots are the evenly spaced Mixon et al. values while the curves represent the Barker method results. 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. The three systems covered in this paper are all well behaved—no mixed deviations—and the level of nonideality changes monotonically with temperature in all cases. As a result, the disagreements between different data reduction procedures are not as sharp as for less well-behaved systems.

Table XV compares the two data reduction methods in terms of accuracy of the P fits. The maximum percent deviation and the root-mean-squared deviation are defined at the bottom of the table. As can be seen from the table, both methods work well for the three systems covered in this paper. However, the Mixon et al. method performed better than the Barker method for six of the nine sets of data. Table XVI further compares the two data reduction methods in terms of the infinite dilution activity coefficients obtained for the diethyl ether + methanol system. Table XVI also shows the values obtained using the Gautreaux–Coates equations (*5*) when the $(dP/dx_1)^\infty$ values needed by those equations come from the cubic splined fits or from the P_D/x_1x_2 or x_1x_2/P_D plots. The estimation of γ_i^∞ values from the plots has been discussed before (*6*). Since the systems are well-behaved, the values obtained by various correlations with the Barker method and by the Gautreaux–Coates method generally agree fairly well with the results of the Mixon et al. method.

Registry No. Acetone, 67-64-1; diethyl ether, 60-29-7; acetonitrile, 75-05-8; methanol, 67-56-1.

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