Total-Pressure Vapor-Liquid Equilibrium Data for Binary Systems of Nitromethane with Ethyl Acetate, Acetonitrile, and Acetone

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Total-pressure vapor-liquid equilibrium (VLE) data are reported at approximately 298, 348, and 398 K for each of three nitromethane binaries with ethyl acetate, acetonitrile, and acetone as the other components. The experimental PTx data were reduced to y_i, γ_i, and G^E values by both the Mixon-Gumowski-Carpenter and the Barker methods, but only the Mixon et al. results are reported in their entirety. Seven G^E correlations were tested in the Barker data reduction with the five-constant Redlich-Kister equation giving the best results. The effect of the equation of state used to estimate the vapor-phase fugacity coefficients was investigated.

Introduction

This paper presents total-pressure vapor-liquid equilibrium data for three systems with nitromethane as the common component. The other components are ethyl acetate, aceto-nitrile, and acetone. Previous papers have reported data for nitromethane with 1-chlorobutane (1) and with chlorobenzene (2). A subsequent paper will cover data with methanol and ethanol. The apparatus and techniques used to measure all of these data have been described previously along with the defining equation for the activity coefficient and the standard state used (3).

Chemicals Used

The sources and purities of the chemicals used are listed in Table I. Activated molecular sieves (either 3A or 4A) were put into the chemical containers as they were received. Just prior to being loaded into 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 verified with gas-liquid chromatography at this point.

None of the compounds exhibited any degradation during the VLE measurements. The cell pressures were stable with respect to time, and all liquids were perfectly clear when removed from the cells at the end of the last isotherm.

Experimental Data

Tables II-IV present the experimental PTx data. The "smooth" pressure values reported are from the least-squares cubic splined fits used to provide the evenly spaced values required by the finite-difference Mixon-Gumowski-Carpenter method (4) for the reduction of PTx data.

Figures 1-3 show the experimental data in terms of the pressure deviation P_D from Raoult's law

$$P_D = P - [P_2' + x_1(P_1' - P_2')]$$

Table I. Chemicals Used

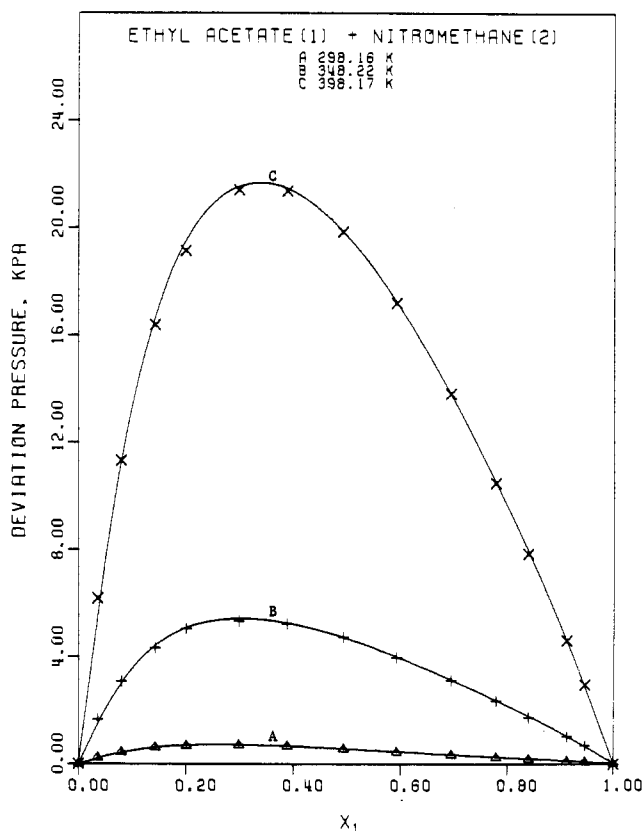| component	vendor	stated purity, %
ethyl acetate	Burdick and Jackson	99.9
acetonitrile	Burdick and Jackson	99.9+
acetone	Burdick and Jackson	99.9+
nitromethane	Mallinckrodt	99.9

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

where P is the experimental mixture pressure and the P_i' values are the pure-component vapor pressures. The deviation pressure plot emphasizes the scatter more than a P vs. x_1 plot but does not show whether or not an azeotrope exists.

The point symbols in Figures 1-3 denote the experimental data points exactly. The curves approximate—sometimes not very closely—the splined fits of those data points. Closely spaced points from the splined fits were fed to the plotting program which then plotted its fit of the input values. The plotting-program fits are often not very good, particularly for a system such as the one in Figure 2. Nevertheless, the curves do help illustrate the behavior and the scatter of the experimental data points. Tables II-IV show how well the splined fits (smooth values) actually do fit the experimental data points.

The ethyl acetate system (Figure 1) exhibited only positive deviations from Raoult's law, while the acetone system (Figure

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

	298.16 K			348.22 K			398.17 K	
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	4.790	4.790	.0000	42.29	42.28	.0000	201.13	201.13
.0360	5.310	5.310	.0359	45.84	45.85	.0359	214.25	214.24
.0802	5.858	5.858	.0802	49.59	49.58	.0801	227.94	227.98
.1429	6.529	6.524	.1428	54.14	54.17	.1427	245.09	245.04
.2007	7.051	7.054	.2006	57.92	57.88	.2004	259.02	259.06
.2990	7.832	7.837	.2989	63.38	63.42	.2987	280.3	280.3
.3892	8.501	8.496	.3890	68.05	68.04	.3887	297.6	297.6
.4937	9.224	9.223	.4936	73.06	73.05	.4933	316.3	316.3
.5933	9.894	9.897	.5931	77.55	77.58	.5929	332.9	333.0
.6952	10.588	10.585	.6951	82.11	82.09	.6948	349.3	349.2
.7795	11.160	11.163	.7794	85.78	85.78	.7792	362.3	362.2
.8404	11.581	11.581	.8404	88.40	88.43	.8402	371.4	371.5
.9124	12.067	12.070	.9124	91.48	91.49	.9123	382.1	382.1
.9465	12.304	12.298	.9465	92.95	92.91	.9465	387.1	387.0
1.0000	12.645	12.647	1.0000	95.06	95.08	1.0000	394.4	394.5

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

|	298.15 K			348.17 K			398.17 K	
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	4.785	4.785	.0000	42.18	42.19	.0000	200.79	200.79
.0476	5.158	5.156	.0476	44.23	44.19	.0475	208.24	208.21
.0949	5.501	5.502	.0949	46.06	46.07	.0948	214.42	214.48
.1462	5.859	5.861	.1461	48.04	48.05	.1461	221.16	221.09
.2147	6.335	6.336	.2145	50.70	50.71	.2145	229.91	229.97
.3010	6.935	6.932	.3009	54.12	54.09	.3008	241.24	241.24
.4094	7.681	7.682	.4094	58.40	58.39	.4092	255.67	255.59
.5068	8.363	8.361	.5067	62.28	62.27	.5066	268.61	268.66
.6021	9.025	9.031	.6021	66.05	65.10	.6019	281.6	281.7
.6941	9.686	9.683	.6940	69.84	69.81	.6939	294.5	294.4
.7819	10.312	10.310	.7819	73.42	73.41	.7818	306.7	306.8
.8612	10.978	10.979	.8612	76.70	76.71	.8611	318.1	318.1
.9253	11.336	11.336	.9253	79.37	79.39	.9253	327.2	327.3
.9618	11.594	11.594	.9618	80.91	80.88	.9618	332.7	332.6
1.0000	11.861	11.861	1.0000	82.36	82.37	1.0000	337.9	338.0
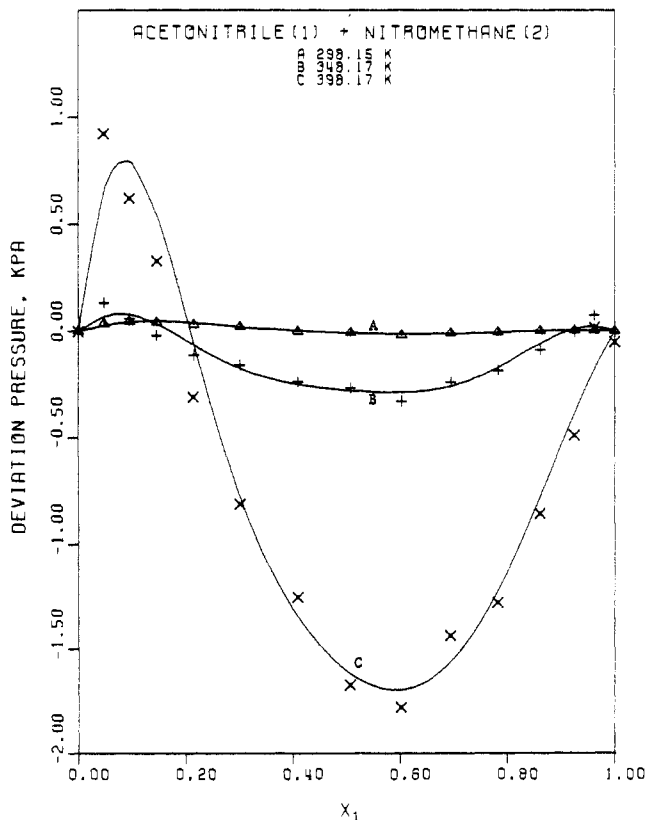
Figure 2. Deviation from Raoult's law for the acetonitrile (1) + nitromethane (2) system.
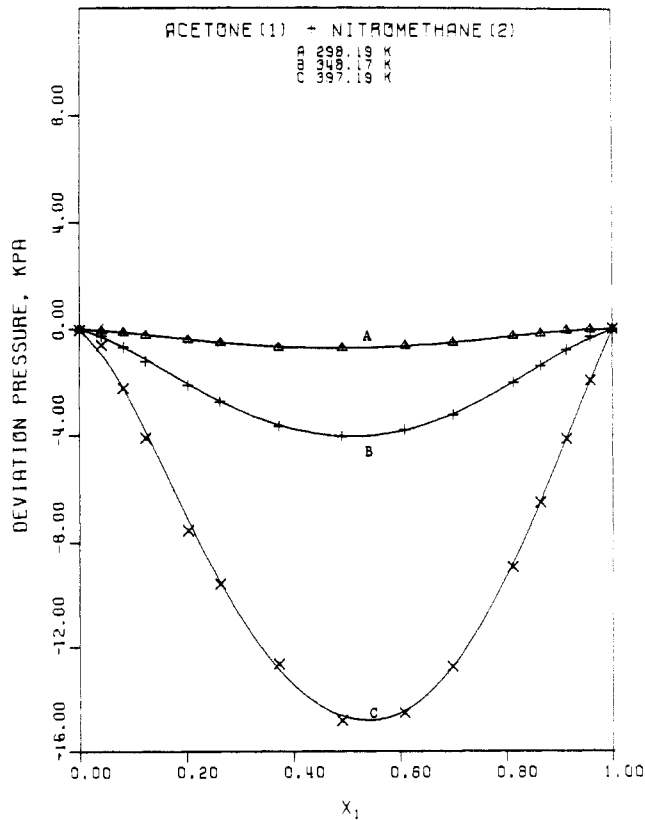

Figure 3. Deviation from Raoult's law for the acetone (1) + nitromethane (2) system.

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

| | 298.19 K | | | 348.17 K | | | 397.19 K | |
| | PRESSURE, KPA | | | PRESSURE, KPA | | | PRESSURE, KPA | |
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	4.790	4.789	.0000	42.15	42.15	.0000	195.31	195.34
.0412	5.811	5.815	.0411	47.82	47.82	.0411	214.01	213.89
.0819	6.804	6.798	.0819	53.28	53.26	.0817	231.47	231.50
.1245	7.801	7.807	.1244	58.84	58.89	.1242	249.49	249.53
.2032	9.689	9.685	.2030	69.29	69.29	.2027	282.9	283.0
.2637	11.153	11.147	.2635	77.39	77.36	.2631	309.2	309.1
.3734	13.840	13.853	.3731	92.25	92.28	.3726	357.5	357.3
.4916	16.889	16.884	.4914	108.93	108.93	.4909	410.8	410.9
.6088	20.029	20.025	.6085	126.06	126.03	.6078	465.9	466.0
.6989	22.511	22.511	.6986	139.60	139.63	.6981	510.1	510.0
.8120	25.686	25.688	.8117	157.12	157.11	.8113	567.0	567.0
.8639	27.153	27.157	.8638	165.25	165.24	.8634	593.8	593.8
.9129	28.54	28.54	.9128	172.91	172.92	.9126	619.3	619.3
.9579	29.77	29.77	.9578	179.91	179.90	.9577	642.7	642.7
1.0000	30.88	30.88	1.0000	186.28	186.29	1.0000	664.4	664.4

Table V. Calculated Data for the Ethyl Acetate (1) + Nitromethane (2) System at 298.16, 348.22, and 398.17 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 98.450   VL(2) = 53.988

X1	TOTAL PRESSURE, KPA EXPTL.	CALC.	MIXTURE FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	EXCESS GIBBS FUNCTION, J/MOLE
.0000	4.790	4.790	.9976	.9980	.0000	1.6156	1.0000	0.00
.1000	6.080	6.080	.9969	.9975	.2848	1.3742	1.0080	96.68
.2000	7.048	7.048	.9964	.9971	.4408	1.2319	1.0274	157.09
.3000	7.845	7.844	.9960	.9967	.5484	1.1369	1.0549	188.25
.4000	8.573	8.573	.9956	.9964	.6359	1.0800	1.0841	196.50
.5000	9.266	9.266	.9953	.9962	.7115	1.0446	1.1139	187.74
.6000	9.942	9.942	.9949	.9959	.7792	1.0224	1.1431	165.65
.7000	10.618	10.618	.9946	.9956	.8415	1.0104	1.1680	133.49
.8000	11.304	11.304	.9942	.9953	.8993	1.0054	1.1851	94.93
.9000	11.986	11.986	.9939	.9951	.9517	1.0025	1.2057	51.94
1.0000	12.647	12.647	.9935	.9948	1.0000	1.0000	1.2895	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 105.858   VL(2) = 57.395

X1	TOTAL PRESSURE, KPA EXPTL.	CALC.	MIXTURE FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	EXCESS GIBBS FUNCTION, J/MOLE
.0000	42.285	42.285	.9860	.9883	.0000	1.5928	1.0000	0.00
.1000	51.103	51.102	.9830	.9858	.2474	1.3522	1.0079	107.90
.2000	57.842	57.840	.9807	.9840	.3977	1.2269	1.0251	175.79
.3000	63.478	63.476	.9788	.9825	.5077	1.1434	1.0492	213.68
.4000	68.579	68.579	.9771	.9811	.5989	1.0908	1.0759	227.66
.5000	73.345	73.345	.9755	.9798	.6785	1.0555	1.1050	222.75
.6000	77.884	77.884	.9739	.9786	.7506	1.0314	1.1364	201.86
.7000	82.305	82.305	.9725	.9774	.8179	1.0163	1.1677	167.45
.8000	86.682	86.682	.9710	.9762	.8817	1.0080	1.1967	122.37
.9000	90.966	90.966	.9696	.9751	.9418	1.0028	1.2333	67.86
1.0000	95.083	95.083	.9682	.9740	1.0000	1.0000	1.3115	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 115.503   VL(2) = 61.451

X1	TOTAL PRESSURE, KPA EXPTL.	CALC.	MIXTURE FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	EXCESS GIBBS FUNCTION, J/MOLE
.0000	201.130	201.130	.9546	.9614	.0000	1.5520	1.0000	0.00
.1000	233.655	233.648	.9471	.9552	.2139	1.3254	1.0075	115.57
.2000	258.961	258.955	.9413	.9505	.3565	1.2156	1.0227	188.69
.3000	280.534	280.529	.9363	.9464	.4672	1.1434	1.0436	231.98
.4000	299.727	299.725	.9319	.9428	.5603	1.0930	1.0690	250.40
.5000	317.477	317.476	.9279	.9395	.6436	1.0586	1.0972	247.87
.6000	334.158	334.157	.9241	.9364	.7204	1.0345	1.1284	227.38
.7000	350.043	350.043	.9205	.9335	.7931	1.0180	1.1624	190.87
.8000	365.407	365.407	.9170	.9307	.8635	1.0081	1.1969	140.27
.9000	380.329	380.330	.9136	.9280	.9321	1.0025	1.2353	77.49
1.0000	394.469	394.469	.9104	.9255	1.0000	1.0000	1.3032	0.00

3) was entirely a negative deviation system at the three temperatures studied. From the trends shown, the ethyl acetate system would probably show negative deviations at lower temperatures, while the acetone system would probably become a positive deviation system. As those two systems pass from one kind of deviation to the other kind, there would be a temperature range in which they would exhibit mixed deviations such as those shown in Figure 2 for acetonitrile.

At 298.15 K, the acetonitrile + nitromethane system shows positive deviations at both ends of the composition range but the P_D curve sags in the middle below the Raoult's law line. It becomes even more "positive" at each end at 348.17 K but the sag in the middle has become more pronounced. At 398.17 K the positive deviation at low x_1 values is stronger but now the system shows only negative deviations in the middle and high x_1 regions.

None of the three systems exhibited an azeotrope at any temperature studied.

Table VI. Calculated Data for the Acetonitrile (1) + Nitromethane (2) System at 298.15, 348.17, and 398.17 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 52.824 VL(2) = 53.942

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	4.785	4.785	.9979	.9980	.0000	1.0893	1.0000	0.00
.1000	5.538	5.538	.9975	.9977	.2198	1.0295	1.0027	13.30
.2000	6.234	6.234	.9972	.9974	.3814	1.0051	1.0066	15.64
.3000	6.925	6.925	.9969	.9971	.5114	0.9976	1.0090	13.85
.4000	7.616	7.616	.9965	.9968	.6186	0.9951	1.0103	10.45
.5000	8.313	8.313	.9963	.9965	.7088	0.9952	1.0102	6.65
.6000	9.016	9.016	.9960	.9962	.7855	0.9965	1.0086	3.26
.7000	9.725	9.725	.9957	.9959	.8512	0.9981	1.0055	0.80
.8000	10.440	10.440	.9953	.9956	.9080	0.9997	1.0005	-0.27
.9000	11.156	11.156	.9950	.9954	.9572	1.0006	0.9958	0.38
1.0000	11.861	11.861	.9947	.9951	1.0000	1.0000	1.0225	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 56.417 VL(2) = 57.211

X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	42.186	42.186	.9875	.9883	.0000	1.0506	1.0000	0.00
.1000	46.274	46.272	.9863	.9872	.1767	1.0044	1.0021	6.76
.2000	50.140	50.138	.9852	.9861	.3226	0.9920	1.0040	4.52
.3000	54.056	54.055	.9840	.9850	.4497	0.9927	1.0037	1.09
.4000	58.016	58.015	.9829	.9839	.5605	0.9946	1.0027	-1.67
.5000	62.006	62.005	.9817	.9828	.6573	0.9960	1.0015	-3.62
.6000	66.014	66.014	.9805	.9817	.7424	0.9969	1.0004	-4.94
.7000	70.057	70.057	.9793	.9806	.8181	0.9979	0.9984	-5.59
.8000	74.159	74.158	.9781	.9795	.8859	0.9996	0.9933	-4.87
.9000	78.337	78.336	.9769	.9783	.9465	1.0014	0.9827	-1.32
1.0000	82.373	82.373	.9757	.9772	1.0000	1.0000	1.0495	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 60.927 VL(2) = 61.112

| X1	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS		Y1	ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
	EXPTL.	CALC.	1	2		1	2	
.0000	200.792	200.792	.9592	.9615	.0000	1.1238	1.0000	0.00
.1000	215.142	215.135	.9563	.9588	.1535	1.0053	1.0046	15.52
.2000	228.076	228.069	.9537	.9563	.2870	0.9934	1.0064	12.45
.3000	241.140	241.134	.9510	.9538	.4081	0.9928	1.0065	7.92
.4000	254.363	254.358	.9484	.9513	.5179	0.9936	1.0061	3.55
.5000	267.774	267.770	.9456	.9487	.6177	0.9949	1.0050	-0.20
.6000	281.400	281.397	.9429	.9461	.7086	0.9964	1.0031	-3.00
.7000	295.256	295.254	.9401	.9435	.7917	0.9980	1.0002	-4.49
.8000	309.354	309.353	.9372	.9408	.8676	0.9994	0.9960	-4.34
.9000	323.699	323.698	.9343	.9381	.9369	1.0004	0.9902	-2.07
1.0000	337.965	337.965	.9315	.9354	1.0000	1.0000	1.0084	0.00
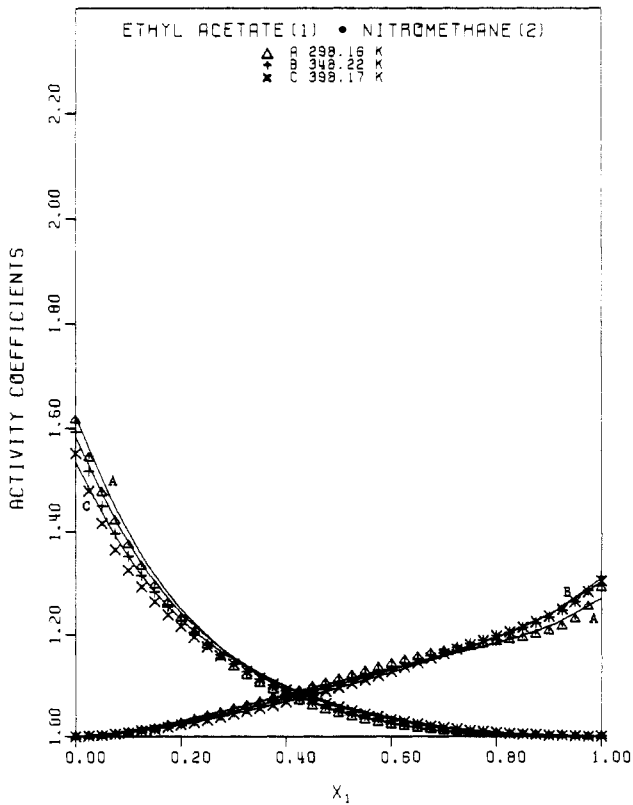
Figure 4. Activity coefficients for the ethyl acetate (1) + nitromethane (2) system. Curves are from Barker method; points are from Mixon et al. method.
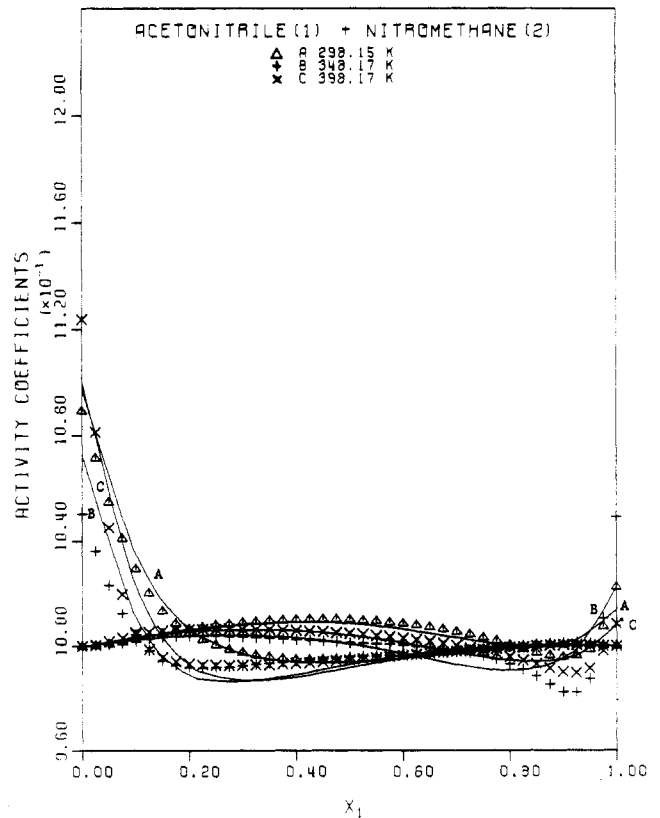

Figure 5. Activity coefficients for the acetonitrile (1) + nitromethane (2) system. Curves are from Barker method; points are from Mixon et al. method. The ×10⁻¹ multiplier means that the decimal must be moved one place to the left in ordinate scale values.

Table VII. Calculated Data for the Acetone (1) + Nitromethane (2) System at 298.19, 348.17, and 397.19 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 74.038   VL(2) = 53.944

| X1 | TOTAL PRESSURE, KPA | | MIXTURE FUGACITY COEFFICIENTS | | Y1 | ACTIVITY COEFFICIENTS | | EXCESS GIBBS FUNCTION, |
	EXPTL.	CALC.	1	2		1	2	J/MOLE
.0000	4.789	4.789	.9981	.9980	.0000	0.9882	1.0000	0.00
.1000	7.227	7.227	.9972	.9970	.4018	0.9499	1.0018	-8.69
.2000	9.609	9.608	.9963	.9960	.5991	0.9404	1.0033	-23.90
.3000	12.033	12.033	.9953	.9950	.7198	0.9424	1.0025	-39.81
.4000	14.524	14.524	.9944	.9939	.8016	0.9490	0.9986	-53.97
.5000	17.104	17.104	.9934	.9929	.8606	0.9589	0.9900	-64.45
.6000	19.784	19.784	.9923	.9918	.9050	0.9708	0.9750	-69.14
.7000	22.542	22.542	.9912	.9906	.9387	0.9824	0.9536	-66.15
.8000	25.350	25.350	.9902	.9894	.9647	0.9922	0.9253	-54.01
.9000	29.176	28.176	.9891	.9883	.9848	0.9995	0.8869	-30.93
1.0000	30.881	30.881	.9880	.9871	1.0000	1.0000	0.9438	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 79.879   VL(2) = 57.211

| X1 | TOTAL PRESSURE, KPA | | MIXTURE FUGACITY COEFFICIENTS | | Y1 | ACTIVITY COEFFICIENTS | | EXCESS GIBBS FUNCTION, |
	EXPTL.	CALC.	1	2		1	2	J/MOLE
.0000	42.147	42.147	.9892	.9883	.0000	1.0144	1.0000	0.00
.1000	55.662	55.660	.9858	.9846	.3146	0.9763	1.0017	-2.62
.2000	68.891	68.888	.9824	.9809	.5049	0.9660	1.0034	-12.21
.3000	82.281	82.279	.9790	.9772	.6357	0.9647	1.0037	-23.70
.4000	96.022	96.020	.9755	.9734	.7319	0.9682	1.0017	-34.51
.5000	110.169	110.168	.9719	.9695	.8054	0.9740	0.9967	-42.91
.6000	124.770	124.768	.9682	.9655	.8631	0.9810	0.9879	-47.43
.7000	139.843	139.843	.9643	.9613	.9093	0.9885	0.9739	-46.47
.8000	155.281	155.280	.9604	.9571	.9464	0.9951	0.9545	-38.42
.9000	170.923	170.923	.9564	.9528	.9762	0.9997	0.9295	-22.01
1.0000	186.286	186.286	.9526	.9485	1.0000	1.0000	0.9593	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 87.528   VL(2) = 61.027

| X1 | TOTAL PRESSURE, KPA | | MIXTURE FUGACITY COEFFICIENTS | | Y1 | ACTIVITY COEFFICIENTS | | EXCESS GIBBS FUNCTION, |
	EXPTL.	CALC.	1	2		1	2	J/MOLE
.0000	195.342	195.342	.9657	.9623	.0000	1.0636	1.0000	0.00
.1000	239.275	239.270	.9580	.9538	.2564	1.0117	1.0023	10.80
.2000	281.865	281.859	.9506	.9457	.4321	0.9954	1.0049	9.95
.3000	325.190	325.185	.9430	.9374	.5546	0.9911	1.0063	5.69
.4000	369.531	369.528	.9353	.9289	.6682	0.9904	1.0067	0.39
.5000	415.154	415.153	.9273	.9201	.7516	0.9916	1.0056	-4.73
.6000	462.271	462.271	.9192	.9112	.8201	0.9939	1.0027	-8.59
.7000	510.934	510.935	.9107	.9019	.8772	0.9966	0.9975	-10.26
.8000	561.165	561.166	.9020	.8923	.9252	0.9992	0.9898	-8.95
.9000	612.778	612.778	.8931	.8824	.9657	1.0009	0.9805	-3.84
1.0000	664.428	664.428	.8842	.8726	1.0000	1.0000	1.0253	0.00

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

component	T_c, K	P_c, MPa	ω
nitromethane	588.0	6.313	0.3460
ethyl acetate	523.2	3.830	0.3630
acetonitrile	548.0	4.833	0.3210
acetone	508.1	4.519	0.3090

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

Reduced Data

The y_i, γ_i, and G^E values selected for publication are given in Tables V–VII. Those values were obtained with the Mixon et al. data reduction method. The Peng–Robinson equation of state (5) was used to estimate the vapor-phase fugacity coefficients. The pure-compound parameters used for the Peng–Robinson equation are in Table VIII.

The "experimental" pressure values tabulated in Tables V–VII 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 method. That method can usually be made to reproduce the input P values to any desired precision.

The PTx data were also reduced with the Barker method (6) using the seven G^E correlations listed in Table IX. As shown there for the acetone + nitromethane system, the five-constant Redlich–Kister equation usually reproduces the experimental P values best followed closely by the modified Margules (8). For this system, very little was lost by using only three instead of five constants in the Redlich–Kister equation. The maximum percent deviation and the root–mean–squared deviation are defined at the bottom of Table X, which gives a more complete comparison of the two data reduction methods insofar as the accuracy of the P fits is concerned. The Barker results in Table X are from the five-constant Redlich–Kister correlation and the Peng–Robinson equation of state (5) was used by both methods. Both methods reproduced the experimental pressure values very well with the Mixon et al. method having the edge in the majority of the cases.

The performances of the two data reduction methods are also compared in Table IX in terms of the infinite-dilution activity coefficients obtained for the acetone + nitromethane system. Also shown are the values obtained with the Gautreaux–Coates equations (9) when the $(dP/dx_1)_i^\infty$ values needed by those equations come from the cubic splined fits or from P_D/x_1x_2 or x_1x_2/P_D plots. The estimation of γ_i^∞ values from the plots has been discussed in a previous paper (10). For this system, the

Table IX. Effect of Calculation Method on γ_i^∞ Values for the Acetone (1) + Nitromethane (2) System[a]

| calculation method | accuracy of P fits, max % dev/rmsd | | | calcd γ_i^∞ values | | | | | |
| | | | | component 1 | | | component 2 | | |
	298.19 K	348.17 K	397.19 K	298.19 K	348.17K	397.19K	298.19K	348.17K	397.19 K
Mixon et al.	0.1/0.0	0.0/0.0	0.1/0.0	0.991	1.016	1.061	0.954	0.966	1.021
Barker:									
absolute Van Laar	1.1/0.5	0.7/0.3	0.6/0.3	0.926	0.959	0.993	0.851	0.906	0.973
Wilson	1.7/0.7	1.0/0.5	0.2/0.1	0.905	0.942	1.047	0.872	0.927	0.976
NRTL	0.3/0.2	0.5/0.2	0.5/0.2	0.991	0.969	1.010	0.880	0.904	0.978
modified Margules	0.1/0.1	0.1/0.0	0.1/0.0	0.975	1.000	1.074	1.130	0.988	1.020
UNIQUAC	2.1/1.0	1.2/0.6	1.0/0.5	0.886	0.931	0.971	0.892	0.940	0.973
Redlich-Kister, three constants	0.2/0.1	0.1/0.1	0.2/0.1	0.983	1.006	1.044	0.871	0.920	0.985
Redlich-Kister, five constants	0.1/0.1	0.1/0.0	0.1/0.0	0.993	1.018	1.068	0.886	0.933	0.999
Gautreaux-Coates:									
splined fits				0.991	1.017	1.062	1.195	1.037	1.047
$x_1 x_2 / P_D$ plots				0.979			1.075		1.042

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

ACETONE (1) + NITROMETHANE (2)
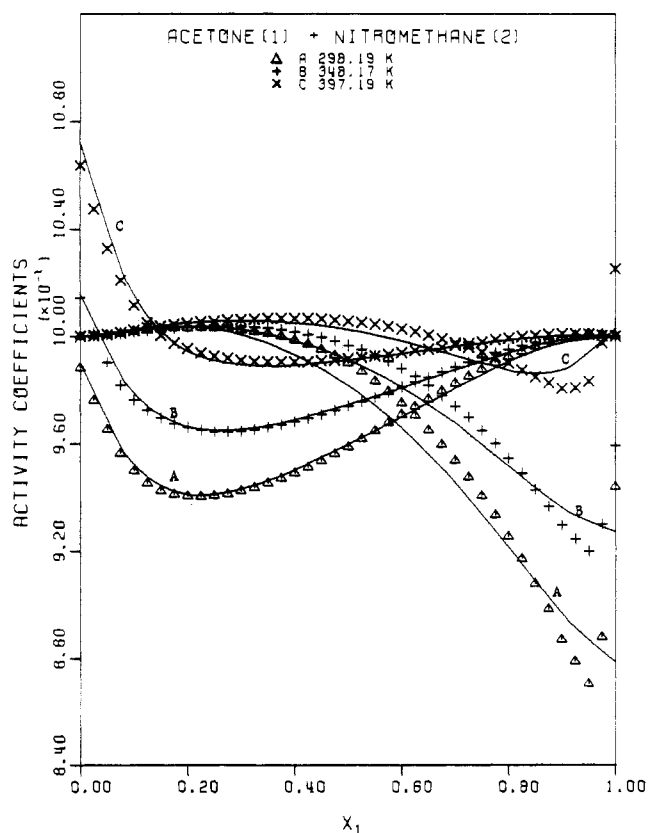△ A 298.19 K
+ B 348.17 K
x C 397.19 K

Figure 6. Activity coefficients for the acetone (1) + nitromethane (2) system. Curves are from Barker method; points are from Mixon et al. method. The ×10⁻¹ multiplier means that the decimal point must be moved one place to the left in ordinate scale values.

extrapolations required in the plots were too uncertain to use in three of the six cases.

Usually the γ_i^∞ values obtained with the Gautreaux-Coates equations agree well with the Mixon et al. values when the splined fits are used to provide $(dP/dx_1)_i^\infty$ values. However, as shown in Table IX for γ_2^∞, that is not always the case. The finite-difference Mixon et al. method "reaches" the $x_1 = 0.0$ and 1.0 points with an extrapolation based on a quadratic fit of the $G^E = 0$ value at $x_1 = 0.0$ or 1.0 plus the two adjacent G^E values. The slope of that quadratic equation can differ from the slope of the cubic splined fits at the end points resulting in different γ_i^∞ values.

It can be seen from Figures 4-6 why the various methods have trouble agreeing on the γ_i^∞ values for some of these systems. The points in those plots are evenly spaced values

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

| temp, K | max % dev in P^a | | rms for % dev[b] | |
	Barker	Mixon	Barker	Mixon
Ethyl Acetate (1) + Nitromethane (2), Peng-Robinson				
298.16	0.126	0.072	0.057	0.038
348.22	0.096	0.065	0.044	0.034
398.17	0.055	0.019	0.020	0.011
Acetonitrile (1) + Nitromethane (2), Peng-Robinson				
298.15	0.047	0.069	0.027	0.028
348.17	0.082	0.082	0.036	0.038
398.17	0.075	0.051	0.036	0.027
Acetone (1) + Nitromethane (2), Peng-Robinson				
298.19	0.108	0.095	0.068	0.048
348.17	0.057	0.045	0.029	0.022
397.19	0.052	0.062	0.027	0.029

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

Table XI. Effect of Equation of State Choice on γ_i^∞ Values Obtained with the Mixon et al. Method for Acetone (1) + Nitromethane (2) at 397.19 K

| eq of state used | γ_i^∞ | |
	1	2
ideal gas	1.001	0.834
virial through B_{ij}:		
Tsonopoulos (7)	1.061	1.021
Hayden-O'Connell (11)	1.125	1.241
Redlich-Kwong: Lu modification (12)	1.062	1.020
Peng-Robinson (5)	1.064	1.025

from the Mixon et al. method while the curves approximate— sometimes closely and sometimes not so closely—the Barker results. Closely spaced values from the Barker calculations are fed to the plotting software which then fits and plots its own representation of those values. In Figure 5, for example, the Barker curves at 348.17 and 398.17 K dip slightly below 0.99 but none of the actual values calculated by the Barker method fall below 0.99.

The ethyl acetate + nitromethane system (Figure 4) is unusual in the small effect of temperature on the activity coefficients. The Mixon et al. and Barker results agree very well for that system. The agreement is not so good for the other two systems, but both methods do give the same reversal in the effect of temperature on γ_1^∞ and γ_2^∞ for the acetonitrile + nitromethane system in Figure 5—the order of the γ_1^∞ values from lowest to highest is 348.17, 298.15, 398.17 K at $x_1 = 0.0$ and 398.17, 298.15, 348.17 K at $x_1 = 1.0$. In Figure 6, the two methods agree fairly well except at high x_1 values. The

Barker method is often less sensitive to the shape of the P vs. x_1 curve near the end points than is the Mixon et al. method. The latter reflects the shapes of the splined fits in that specific region while the former reflects the values of the G^E correlation constants obtained from a fit of all the data points across the entire composition range.

The activity coefficient values (as well as the y_i and G^E values) obtained are a function also of the equation of state used to estimate the vapor-phase fugacity coefficients. Table XI shows the effect of assuming ideal gases for the acetone + nitromethane system at 397.19 K where the pressure ranged from 195 to 665 kPa. The other three equations of state tested showed surprising agreement when the Tsonopoulos (7) correlation is used to estimate the B values for the virial equation.

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Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of Nitromethane with Methanol and Ethanol

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Total-pressure vapor–liquid equilibrium (VLE) data are reported at approximately 298, 348, and 388 K for methanol + nitromethane and at approximately 298, 348, and 398 K for ethanol + nitromethane. The experimental PTx data were reduced to y_i, γ_i, and G^E values by both the Mixon–Gumowski–Carpenter and the Barker methods, but only the Mixon et al. results are reported in their entirety. Seven G^E correlations were tested in the Barker data reduction; the five-constant Redlich–Kister equation gave the best results. The effect of the equation of state choice was investigated.

Introduction

This paper presents total-pressure vapor–liquid equilibrium (VLE) data for nitromethane with methanol and ethanol. Previous papers have reported data for nitromethane with 1-chlorobutane (1), with chlorobenzene (2), and with ethyl acetate, acetonitrile, and acetone (3). The apparatus and techniques used to measure all of these data have been described previously along with the defining equation for the activity coefficient and the standard states used (4).

Chemicals Used

The sources and the purities of the chemicals used are listed in Table I. Activated molecular sieves (either 3A or 4A) were put into the chemical containers as they were received. Just prior to being loaded into 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

Table I. Chemicals Used

component	vendor	stated purity, %
ethanol	U.S. Industrial Chemicals	200 proof
methanol	Fisher Scientific	99.9
nitromethane	Mallinckrodt	99.9

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 verified with gas–liquid chromatography at this point.

None of the compounds exhibited any degradation during the VLE measurements. The cell pressures were stable with respect to time, and all liquids were perfectly clear when removed from the cells at the end of the last isotherm.

Experimental Data

Tables II and III present the experimental PTx data. The "smooth" pressure values reported are from the least-squares cubic splined fits used to provide the evenly spaced values required by the finite-difference Mixon–Gumowski–Carpenter method (5) for the reduction of PTx data.

Figures 1 and 2 show the experimental data in terms of the pressure deviation P_D from Raoult's law

$$P_D = P - [P_2' + x_1(P_1' - P_2')]$$

where P is the experimental mixture pressure and the P_i' values are the pure-component vapor pressures. The deviation pressure plot emphasizes the scatter more than the P vs. x_1 plot but does not show whether or not any azeotrope exists.

The point symbols in Figures 1 and 2 denote the experimental data points exactly. The curves approximate—in these cases quite closely—the splined fits of those data points. For an