Total Pressure Vapor–Liquid Equilibrium Data for Benzene + Acetonitrile, Diethylamine + Ethyl Acetate, and Propylamine + Diethylamine Binary Systems

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Total pressure vapor–liquid equilibrium (VLE) data are reported at 298, 348, and 398 K for the benzene + acetonitrile and diethylamine + ethyl acetate binaries, and at 298 and 348 K for the propylamine + diethylamine binary. 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. Various equations of state were used to estimate vapor-phase fugacity coefficients; the Peng–Robinson results were used for the values reported. The effect of small errors in the experimental pressure values on the shapes of the activity coefficient curves is illustrated.

Introduction

In 1977 it was estimated that vapor–liquid equilibrium (VLE) data were needed for about 160 binary pairs to fill the gaps in the UNIFAC parameter table published that year (1). It was further estimated that about 50–60 of those 160 systems would have to be studied in a PTxy apparatus (equilibrium phases sampled and analyzed) while the remaining 100–110 systems could best be handled in total pressure (PTx) devices.

The criterion for classifying each system as either a PTxy or PTx system was the accuracy with which the vapor-phase fugacity coefficients could be predicted with an ordinary equation of state (virial, Redlich–Kwong, Peng–Robinson, BWR, etc.). The y values calculated from the total pressure (PTx) data are

Table I. Chemicals Used

component	vendor	purity, %
benzene	Burdick and Jackson	99.9+
acetonitrile	Burdick and Jackson	99.9+
diethylamine	Sigma Chemicals	99.9
ethylacetate	Burdick and Jackson	99.9
propylamine	Sigma Chemicals	99.9

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

	298.16 K			348.03 K			397.86 K	
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	11.787	11.786	0.0	81.45	81.44	0.0	335.1	335.1
0.0446	12.895	12.901	0.0445	87.44	87.47	0.0444	353.7	353.9
0.0838	13.607	13.598	0.0837	91.51	91.46	0.0835	367.1	366.9
0.1432	14.387	14.384	0.1430	96.12	96.11	0.1427	382.5	382.5
0.2114	14.991	15.001	0.2111	99.87	99.92	0.2109	395.3	395.5
0.3010	15.495	15.492	0.3009	103.15	103.12	0.3007	406.6	406.6
0.4007	15.805	15.803	0.4006	105.19	105.18	0.4005	413.4	413.3
0.5033	15.941	15.940	0.5033	106.03	106.04	0.5033	415.5	415.5
0.6014	15.912	15.919	0.6015	105.81	105.81	0.6017	413.4	413.7
0.6975	15.741	15.731	0.6976	104.57	104.55	0.7001	407.3	407.2
0.7848	15.360	15.371	0.7850	102.28	102.30	0.7853	396.8	396.9
0.8572	14.876	14.866	0.8573	99.15	99.15	0.8577	384.1	383.8
0.9138	14.288	14.296	0.9139	95.58	95.55	0.9141	369.8	370.3
0.9498	13.817	13.814	0.9499	92.49	92.51	0.9502	359.8	359.5
1.0000	12.728	12.728	1.0000	86.12	86.12	1.0000	335.4	335.5

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

	297.98 K			348.09 K			398.03 K	
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	12.570	12.575	0.0	94.62	94.62	0.0	392.0	392.0
0.0326	13.594	13.583	0.0325	99.25	99.25	0.0323	404.5	404.5
0.0852	15.051	15.059	0.0850	106.27	106.26	0.0847	424.3	424.3
0.1469	16.614	16.618	0.1466	113.90	113.91	0.1463	446.6	446.6
0.2160	18.260	18.247	0.2157	122.02	122.02	0.2153	470.2	470.3
0.3030	20.126	20.137	0.3027	131.57	131.56	0.3023	498.4	498.3
0.4004	22.035	22.029	0.3999	141.31	141.33	0.3994	527.5	527.5
0.5012	23.812	23.812	0.5009	150.71	150.69	0.5005	555.9	555.9
0.6038	25.515	25.520	0.6036	159.57	159.58	0.6033	583.1	583.1
0.7014	27.063	27.058	0.7012	167.54	167.54	0.7009	607.2	607.2
0.7779	28.20	28.21	0.7777	173.49	173.48	0.7774	625.0	625.1
0.8577	29.36	29.36	0.8576	179.43	179.44	0.8574	643.0	643.0
0.9204	30.26	30.26	0.9203	183.99	183.98	0.9202	656.6	656.6
0.9554	30.76	30.76	0.9554	186.48	186.48	0.9553	663.8	663.9
1.0000	31.39	31.39	1.0000	189.63	189.63	1.0000	672.7	672.6

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

	297.97 K			347.96 K	
	P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	31.41	31.41	0.0	188.89	188.89
0.0355	31.88	31.88	0.0354	191.58	191.57
0.0627	32.24	32.24	0.0626	193.60	193.61
0.1356	33.18	33.18	0.1355	198.91	198.92
0.2033	34.03	34.03	0.2032	203.68	203.68
0.2937	35.11	35.12	0.2936	209.81	209.81
0.3983	36.31	36.31	0.3981	216.56	216.58
0.4951	37.37	37.37	0.4947	222.57	222.57
0.6017	38.47	38.47	0.6015	228.91	228.90
0.6979	39.41	39.41	0.6978	234.35	234.35
0.7892	40.27	40.27	0.7891	239.32	239.32
0.8578	40.91	40.92	0.8577	242.98	242.98
0.9187	41.49	41.49	0.9186	246.18	246.19
0.9578	41.84	41.84	0.9578	248.14	248.13
1.0000	42.17	42.17	1.0000	250.02	250.03

Table V. Calculated Data for the Benzene (1) + Acetonitrile (2) System at 298.16 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 89.41   COMPONENT 2 = 52.82

|	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	11.786	11.786	0.9949	0.9947	0.0	3.2827	1.0000	0.0
0.050	13.010	13.009	0.9943	0.9942	0.1350	2.7603	1.0044	136.20
0.100	13.839	13.839	0.9940	0.9938	0.2208	2.3993	1.0156	251.50
0.150	14.458	14.458	0.9937	0.9935	0.2844	2.1522	1.0314	350.19
0.200	14.916	14.915	0.9935	0.9933	0.3333	1.9508	1.0531	433.97
0.250	15.247	15.247	0.9933	0.9932	0.3720	1.7803	1.0815	503.04
0.300	15.488	15.488	0.9932	0.9931	0.4045	1.6385	1.1160	557.63
0.350	15.669	15.669	0.9932	0.9930	0.4343	1.5255	1.1550	598.55
0.400	15.802	15.802	0.9931	0.9929	0.4624	1.4331	1.1990	626.79
0.450	15.890	15.890	0.9931	0.9929	0.4894	1.3556	1.2493	642.86
0.500	15.938	15.938	0.9930	0.9929	0.5166	1.2917	1.3050	647.14
0.550	15.949	15.949	0.9930	0.9929	0.5452	1.2401	1.3651	640.65
0.600	15.920	15.921	0.9931	0.9929	0.5718	1.1903	1.4431	622.85
0.650	15.847	15.847	0.9931	0.9929	0.6001	1.1478	1.5333	592.97
0.700	15.723	15.723	0.9931	0.9930	0.6308	1.1117	1.6387	551.03
0.750	15.542	15.542	0.9932	0.9931	0.6647	1.0807	1.7656	496.61
0.800	15.283	15.283	0.9933	0.9932	0.7040	1.0554	1.9158	429.26
0.850	14.926	14.926	0.9935	0.9933	0.7513	1.0354	2.0967	348.69
0.900	14.451	14.450	0.9937	0.9936	0.8088	1.0195	2.3410	253.91
0.950	13.811	13.810	0.9940	0.9938	0.8811	1.0058	2.7841	140.57
1.000	12.728	12.728	0.9944	0.9943	1.0000	1.0000	3.5005	0.0
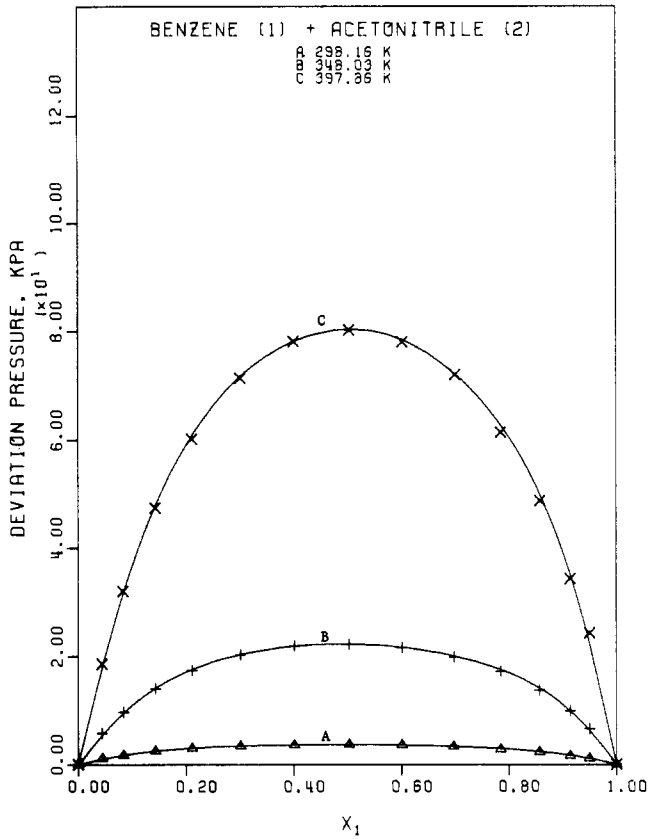
Figure 1. Deviations from Raoult's law for the benzene (1) + acetonitrile (2) system. Ordinate values run from 0.0 to 120.0.
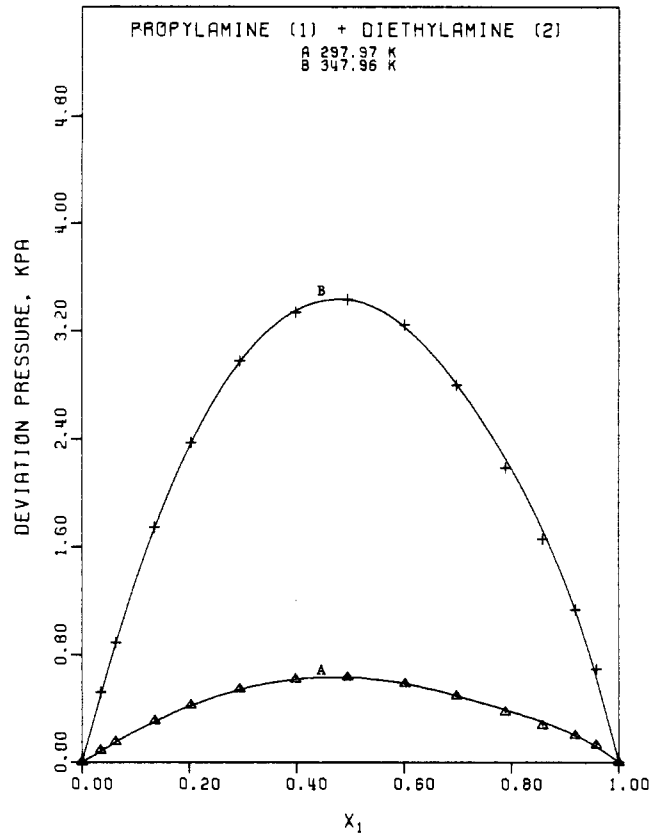

Figure 3. Deviations from Raoult's law for the propylamine (1) + diethylamine (2) system.
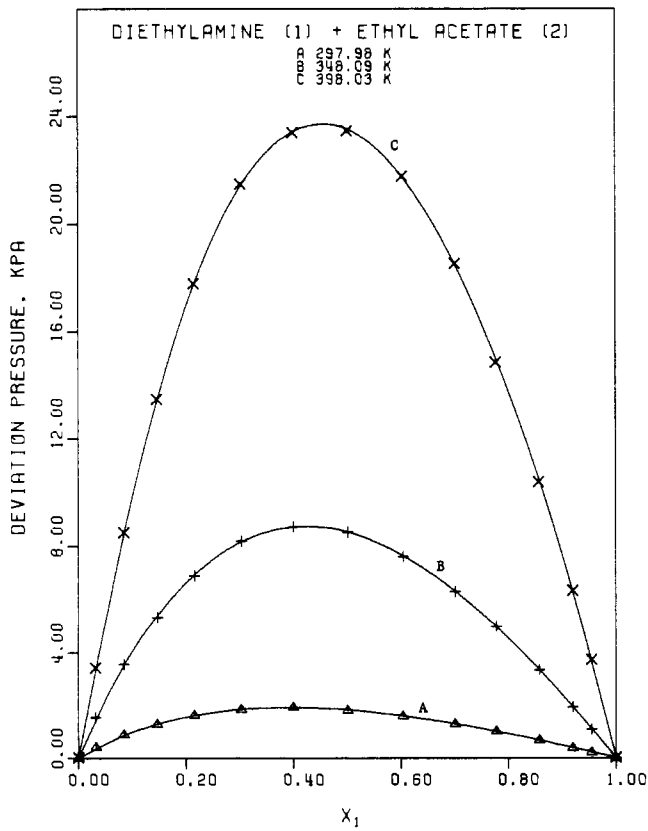

Figure 2. Deviations from Raoult's law for the diethylamine (1) + ethyl acetate (2) system.
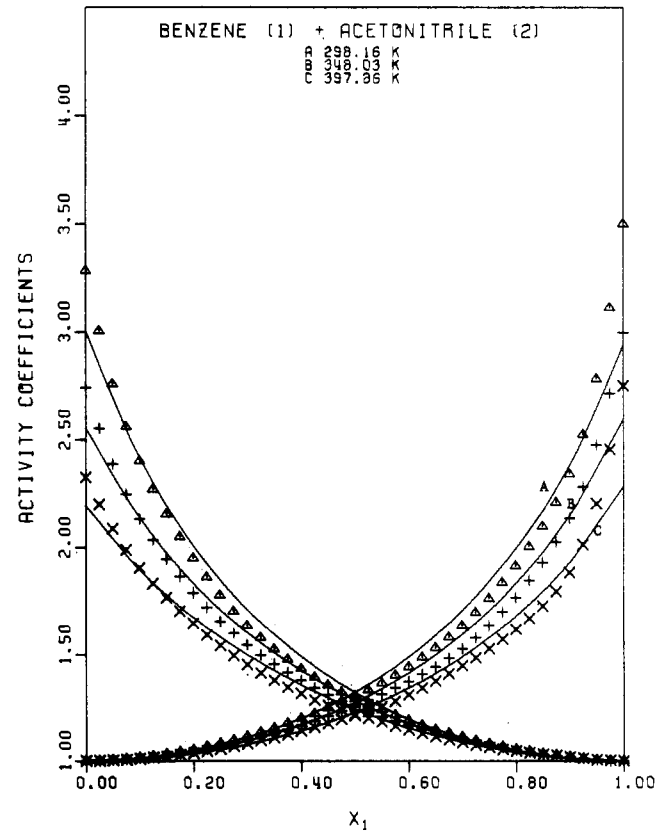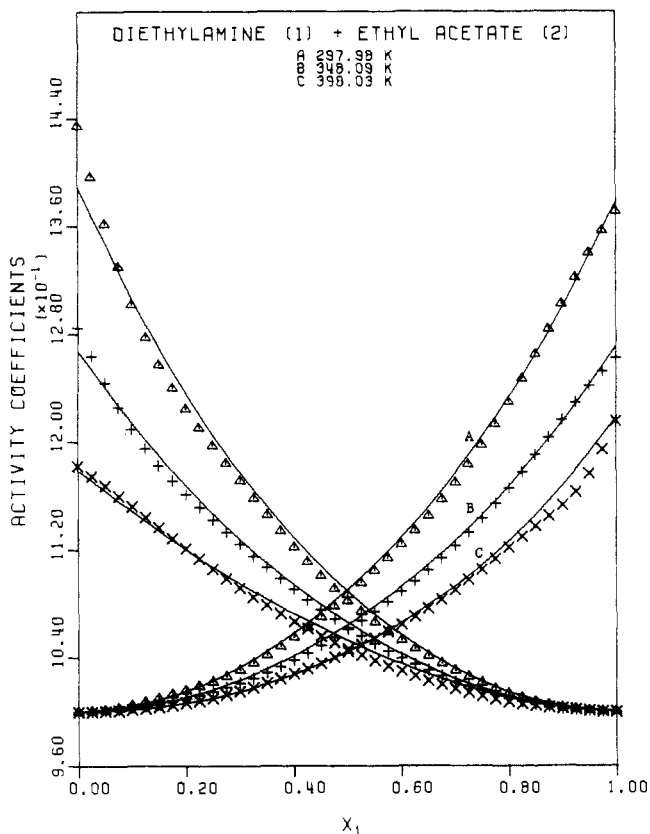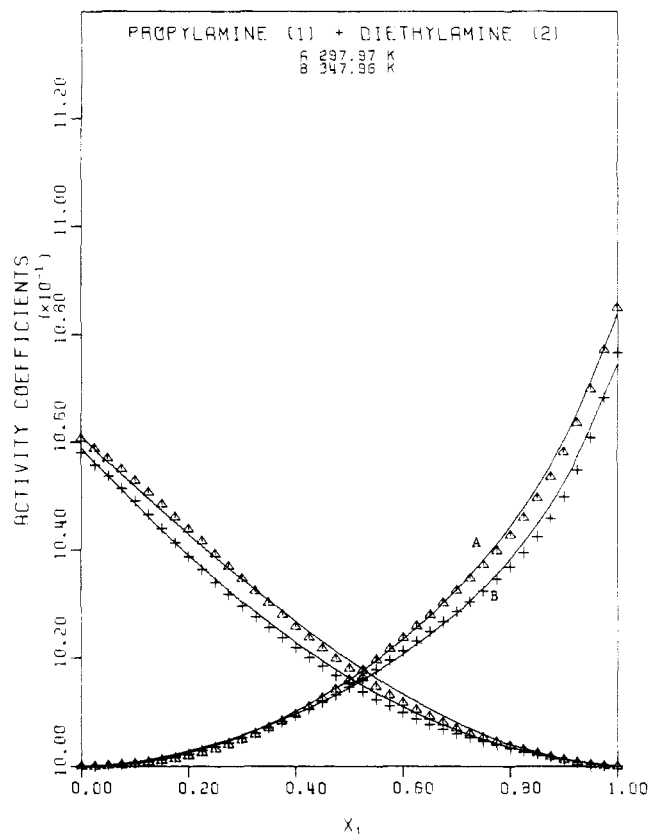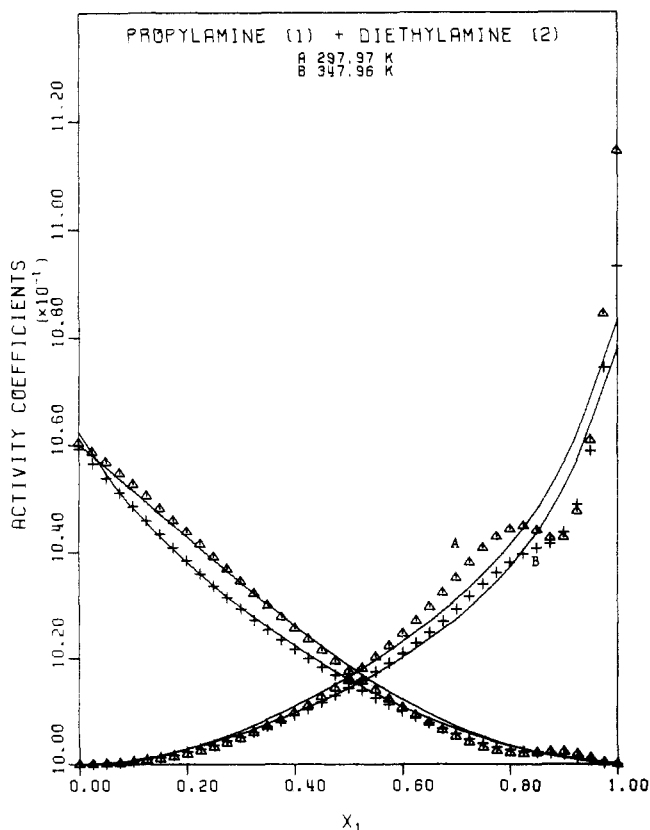

Figure 4. Activity coefficients for the benzene (1) + acetonitrile (2) system. Curves from Barker results, points from Mixon et al. method.

Figure 5. Activity coefficients for the diethylamine (1) + ethyl acetate (2) system. Curves from Barker results; points from Mixon et al. method.

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

Figure 7. Activity coefficients for the propylamine (1) + diethylamine (2) system; modified pressures.

Table VI. Calculated Data for the Benzene (1) + Acetonitrile (2) System at 348.03 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 95.32   COMPONENT 2 = 56.41

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	81.444	81.444	0.9761	0.9759	0.0	2.7429	1.0000	0.0
0.050	88.091	88.090	0.9741	0.9740	0.1167	2.3851	1.0035	135.49
0.100	92.878	92.877	0.9727	0.9726	0.1979	2.1293	1.0126	251.33
0.150	96.571	96.572	0.9717	0.9715	0.2611	1.9452	1.0257	351.27
0.200	99.391	99.393	0.9708	0.9706	0.3117	1.7910	1.0438	436.60
0.250	101.509	101.512	0.9702	0.9700	0.3535	1.6582	1.0675	507.50
0.300	103.096	103.100	0.9697	0.9695	0.3896	1.5459	1.0962	564.14
0.350	104.301	104.305	0.9694	0.9692	0.4228	1.4543	1.1288	607.24
0.400	105.175	105.179	0.9691	0.9689	0.4540	1.3773	1.1663	637.57
0.450	105.743	105.747	0.9690	0.9688	0.4835	1.3106	1.2099	655.39
0.500	106.032	106.036	0.9689	0.9687	0.5123	1.2532	1.2598	660.72
0.550	106.061	106.064	0.9689	0.9687	0.5426	1.2069	1.3133	654.15
0.600	105.825	105.828	0.9689	0.9687	0.5739	1.1677	1.3733	636.30
0.650	105.310	105.314	0.9691	0.9689	0.6064	1.1335	1.4431	607.15
0.700	104.505	104.508	0.9693	0.9691	0.6399	1.1025	1.5287	566.20
0.750	103.367	103.368	0.9697	0.9695	0.6750	1.0741	1.6381	512.17
0.800	101.763	101.763	0.9701	0.9699	0.7147	1.0501	1.7710	443.89
0.850	99.539	99.538	0.9708	0.9706	0.7617	1.0311	1.9300	360.82
0.900	96.540	96.537	0.9717	0.9715	0.8190	1.0165	2.1350	262.16
0.950	92.503	92.499	0.9729	0.9727	0.8907	1.0049	2.4740	144.41
1.000	86.121	86.121	0.9747	0.9746	1.0000	1.0000	2.9978	0.0

affected by the accuracy of the predicted vapor-phase fugacity coefficients. On the other hand, the *y* values obtained from a *PTxy* apparatus are inaccurate to some level due to the experimental difficulties involved in capturing an equilibrium phase sample, transporting that sample to the analytical device without changing its composition, and then analyzing it. When the *y*-value errors related to sampling and analyzing are larger than those due to errors in the predicted vapor-phase fugacity coefficients, the system is best studied on a *PTx* apparatus. Since it is very difficult experimentally to sample and analyze phase samples accurately, the *PTx* approach (where the phase analysis errors are eliminated) should be the preferred method for at least two-thirds of the 160 systems needed in 1977.

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Table VII. Calculated Data for the Benzene (1) + Acetonitrile (2) System at 397.86 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 102.40   COMPONENT 2 = 61.04

X1	P, KPA EXPTL	CALC	FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	GE J/MOL
0.0	335.068	335.068	0.9313	0.9319	0.0	2.3233	1.0000	0.0
0.050	355.904	355.906	0.9270	0.9277	0.0988	2.0847	1.0027	130.13
0.100	371.698	371.702	0.9238	0.9245	0.1735	1.9050	1.0100	242.75
0.150	384.125	384.130	0.9213	0.9220	0.2342	1.7665	1.0209	340.50
0.200	393.753	393.758	0.9193	0.9201	0.2847	1.6468	1.0362	424.16
0.250	401.056	401.061	0.9178	0.9186	0.3278	1.5420	1.0562	493.76
0.300	406.506	406.510	0.9167	0.9175	0.3659	1.4520	1.0805	549.41
0.350	410.518	410.521	0.9159	0.9167	0.4014	1.3773	1.1083	591.73
0.400	413.271	413.276	0.9153	0.9161	0.4351	1.3141	1.1400	621.42
0.450	414.884	414.888	0.9150	0.9158	0.4678	1.2604	1.1756	638.86
0.500	415.473	415.475	0.9149	0.9157	0.5018	1.2183	1.2121	644.79
0.550	415.119	415.122	0.9150	0.9157	0.5356	1.1813	1.2545	640.54
0.600	413.724	413.727	0.9153	0.9160	0.5676	1.1439	1.3103	624.41
0.650	411.135	411.138	0.9158	0.9165	0.6008	1.1115	1.3745	595.61
0.700	407.199	407.202	0.9166	0.9173	0.6368	1.0846	1.4463	554.24
0.750	401.747	401.751	0.9177	0.9184	0.6765	1.0624	1.5273	500.42
0.800	394.555	394.559	0.9192	0.9199	0.7210	1.0445	1.6195	434.16
0.850	385.380	385.385	0.9210	0.9217	0.7717	1.0301	1.7297	355.18
0.900	373.982	373.983	0.9233	0.9240	0.8296	1.0177	1.8849	262.04
0.950	359.529	359.527	0.9263	0.9270	0.8967	1.0056	2.2031	148.24
1.000	335.451	335.451	0.9312	0.9318	1.0000	1.0000	2.7524	0.0

Table X. Calculated Data for the Diethylamine (1) + Ethyl Acetate (2) System at 398.03 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 125.45   COMPONENT 2 = 115.98

X1	P, KPA EXPTL	CALC	FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	GE J/MOL
0.0	392.022	392.022	0.9230	0.9109	0.0	1.1821	1.0000	0.0
0.050	411.271	411.273	0.9192	0.9066	0.0892	1.1671	1.0003	26.62
0.100	429.899	429.899	0.9155	0.9024	0.1693	1.1519	1.0014	50.98
0.150	447.853	447.849	0.9119	0.8984	0.2415	1.1363	1.0034	72.88
0.200	465.100	465.095	0.9085	0.8945	0.3072	1.1207	1.0063	92.10
0.250	481.667	481.660	0.9053	0.8908	0.3674	1.1058	1.0102	108.49
0.300	497.594	497.585	0.9021	0.8873	0.4231	1.0917	1.0152	121.99
0.350	512.922	512.913	0.8991	0.8839	0.4750	1.0786	1.0211	132.54
0.400	527.699	527.689	0.8962	0.8806	0.5237	1.0666	1.0280	140.14
0.450	541.975	541.966	0.8934	0.8774	0.5699	1.0558	1.0357	144.77
0.500	555.801	555.792	0.8907	0.8743	0.6140	1.0461	1.0444	146.49
0.550	569.216	569.209	0.8881	0.8714	0.6564	1.0375	1.0539	145.32
0.600	582.225	582.218	0.8855	0.8685	0.6973	1.0299	1.0645	141.29
0.650	594.821	594.815	0.8830	0.8657	0.7369	1.0230	1.0765	134.36
0.700	606.998	606.992	0.8807	0.8630	0.7754	1.0169	1.0901	124.42
0.750	618.762	618.760	0.8783	0.8604	0.8132	1.0115	1.1054	111.33
0.800	630.178	630.177	0.8761	0.8579	0.8506	1.0073	1.1216	95.08
0.850	641.326	641.324	0.8739	0.8555	0.8880	1.0042	1.1374	75.83
0.900	652.249	652.248	0.8718	0.8531	0.9253	1.0023	1.1528	53.98
0.950	662.773	662.774	0.8698	0.8508	0.9624	1.0008	1.1759	29.30
1.000	672.642	672.642	0.8678	0.8487	1.0000	1.0000	1.2152	0.0

Table VIII. Calculated Data for the Diethylamine (1) + Ethyl Acetate (2) System at 297.98 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 104.18   COMPONENT 2 = 98.42

X1	P, KPA EXPTL	CALC	FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	GE J/MOL
0.0	12.575	12.575	0.9945	0.9936	0.0	1.4344	1.0000	0.0
0.050	14.091	14.090	0.9938	0.9928	0.1503	1.3612	1.0013	41.32
0.100	15.445	15.445	0.9932	0.9921	0.2625	1.3016	1.0049	76.25
0.150	16.694	16.694	0.9926	0.9915	0.3519	1.2567	1.0099	105.66
0.200	17.881	17.880	0.9921	0.9909	0.4270	1.2242	1.0155	130.70
0.250	19.009	19.009	0.9916	0.9903	0.4910	1.1966	1.0222	152.03
0.300	20.075	20.075	0.9911	0.9897	0.5462	1.1707	1.0308	169.69
0.350	21.076	21.076	0.9907	0.9892	0.5941	1.1455	1.0416	183.49
0.400	22.022	22.021	0.9902	0.9888	0.6367	1.1218	1.0548	193.21
0.450	22.923	22.922	0.9898	0.9883	0.6753	1.1005	1.0699	198.76
0.500	23.790	23.790	0.9895	0.9879	0.7111	1.0818	1.0865	200.22
0.550	24.635	24.635	0.9891	0.9874	0.7446	1.0660	1.1043	197.74
0.600	25.458	25.458	0.9887	0.9870	0.7764	1.0525	1.1236	191.50
0.650	26.258	26.258	0.9884	0.9866	0.8067	1.0407	1.1449	181.55
0.700	27.036	27.036	0.9880	0.9862	0.8356	1.0302	1.1691	167.83
0.750	27.792	27.792	0.9877	0.9858	0.8634	1.0210	1.1972	150.16
0.800	28.529	28.529	0.9873	0.9855	0.8907	1.0133	1.2291	128.35
0.850	29.254	29.253	0.9870	0.9851	0.9177	1.0072	1.2645	102.30
0.900	29.970	29.969	0.9867	0.9847	0.9448	1.0030	1.3022	72.01
0.950	30.681	30.681	0.9864	0.9844	0.9723	1.0006	1.3396	37.70
1.000	31.392	31.392	0.9861	0.9840	1.0000	1.0000	1.3706	0.0

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

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 82.98   COMPONENT 2 = 104.14

X1	P, KPA EXPTL	CALC	FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	GE J/MOL
0.0	31.412	31.412	0.9898	0.9861	0.0	1.0604	1.0000	0.0
0.050	32.073	32.073	0.9895	0.9858	0.0692	1.0568	1.0001	7.06
0.100	32.723	32.723	0.9893	0.9855	0.1352	1.0527	1.0004	13.64
0.150	33.360	33.361	0.9890	0.9852	0.1981	1.0483	1.0010	19.67
0.200	33.984	33.985	0.9888	0.9849	0.2582	1.0438	1.0019	25.06
0.250	34.594	34.594	0.9886	0.9847	0.3157	1.0391	1.0032	29.78
0.300	35.189	35.189	0.9884	0.9844	0.3709	1.0345	1.0049	33.76
0.350	35.769	35.769	0.9882	0.9842	0.4239	1.0299	1.0071	36.95
0.400	36.334	36.334	0.9880	0.9840	0.4750	1.0256	1.0097	39.31
0.450	36.884	36.885	0.9878	0.9837	0.5244	1.0214	1.0127	40.81
0.500	37.421	37.421	0.9876	0.9835	0.5723	1.0175	1.0162	41.43
0.550	37.944	37.944	0.9874	0.9833	0.6188	1.0140	1.0202	41.14
0.600	38.453	38.453	0.9872	0.9831	0.6641	1.0107	1.0246	39.91
0.650	38.948	38.949	0.9870	0.9829	0.7083	1.0078	1.0296	37.75
0.700	39.431	39.432	0.9869	0.9827	0.7517	1.0052	1.0351	34.60
0.750	39.903	39.903	0.9867	0.9825	0.7944	1.0031	1.0407	30.49
0.800	40.370	40.370	0.9865	0.9823	0.8368	1.0021	1.0443	25.59
0.850	40.841	40.841	0.9864	0.9822	0.8790	1.0021	1.0441	20.39
0.900	41.319	41.318	0.9862	0.9820	0.9204	1.0023	1.0427	15.52
0.950	41.775	41.774	0.9861	0.9818	0.9599	1.0011	1.0608	9.98
1.000	42.169	42.169	0.9859	0.9817	1.0000	1.0000	1.1144	0.0

Table IX. Calculated Data for the Diethylamine (1) + Ethyl Acetate (2) System at 348.09 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 113.04   COMPONENT 2 = 105.95

X1	P, KPA EXPTL	CALC	FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	GE J/MOL
0.0	94.622	94.622	0.9726	0.9683	0.0	1.2849	1.0000	0.0
0.050	101.652	101.648	0.9706	0.9660	0.1126	1.2437	1.0008	33.83
0.100	108.167	108.165	0.9687	0.9638	0.2062	1.2093	1.0031	63.00
0.150	114.316	114.313	0.9669	0.9618	0.2866	1.1821	1.0063	88.09
0.200	120.211	120.209	0.9652	0.9598	0.3576	1.1608	1.0102	109.76
0.250	125.865	125.862	0.9635	0.9579	0.4208	1.1420	1.0150	128.35
0.300	131.270	131.266	0.9619	0.9562	0.4775	1.1241	1.0211	143.85
0.350	136.421	136.416	0.9604	0.9545	0.5287	1.1067	1.0288	156.10
0.400	141.341	141.336	0.9590	0.9528	0.5755	1.0903	1.0381	164.94
0.450	146.060	146.054	0.9576	0.9513	0.6189	1.0752	1.0488	170.29
0.500	150.608	150.603	0.9563	0.9498	0.6595	1.0617	1.0608	172.14
0.550	155.011	155.006	0.9550	0.9483	0.6981	1.0499	1.0741	170.55
0.600	159.281	159.276	0.9538	0.9469	0.7348	1.0394	1.0887	165.55
0.650	163.424	163.419	0.9526	0.9456	0.7701	1.0303	1.1049	157.14
0.700	167.447	167.442	0.9514	0.9442	0.8042	1.0222	1.1230	145.29
0.750	171.357	171.353	0.9503	0.9430	0.8375	1.0154	1.1431	129.92
0.800	175.166	175.163	0.9492	0.9417	0.8701	1.0097	1.1654	110.97
0.850	178.882	178.880	0.9481	0.9405	0.9025	1.0053	1.1899	88.40
0.900	182.519	182.518	0.9471	0.9393	0.9348	1.0022	1.2159	62.19
0.950	186.096	186.095	0.9460	0.9381	0.9673	1.0005	1.2413	32.52
1.000	189.633	189.633	0.9450	0.9370	1.0000	1.0000	1.2621	0.0

Table XII. Calculated Data for the Propylamine (1) + Diethylamine (2) System at 347.96 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 89.88   COMPONENT 2 = 113.00

X1	P, KPA EXPTL	CALC	FUGACITY COEFFICIENTS 1	2	Y1	ACTIVITY COEFFICIENTS 1	2	GE J/MOL
0.0	188.889	188.889	0.9594	0.9452	0.0	1.0593	1.0000	0.0
0.050	192.665	192.668	0.9584	0.9441	0.0673	1.0539	1.0001	7.95
0.100	196.354	196.358	0.9575	0.9430	0.1315	1.0487	1.0005	15.14
0.150	199.954	199.958	0.9566	0.9420	0.1930	1.0434	1.0013	21.53
0.200	203.463	203.469	0.9558	0.9410	0.2519	1.0384	1.0023	27.07
0.250	206.887	206.894	0.9549	0.9401	0.3086	1.0336	1.0036	31.76
0.300	210.231	210.238	0.9541	0.9392	0.3632	1.0293	1.0052	35.59
0.350	213.499	213.507	0.9533	0.9383	0.4160	1.0253	1.0071	38.59
0.400	216.703	216.703	0.9526	0.9374	0.4672	1.0216	1.0093	40.77
0.450	219.823	219.830	0.9518	0.9366	0.5169	1.0183	1.0117	42.12
0.500	222.883	222.890	0.9511	0.9358	0.5653	1.0153	1.0144	42.66
0.550	225.880	225.886	0.9504	0.9350	0.6124	1.0125	1.0175	42.37
0.600	228.811	228.816	0.9497	0.9342	0.6584	1.0100	1.0209	41.26
0.650	231.676	231.680	0.9490	0.9335	0.7034	1.0077	1.0248	39.28
0.700	234.474	234.478	0.9484	0.9327	0.7475	1.0057	1.0292	36.40
0.750	237.208	237.211	0.9478	0.9321	0.7909	1.0039	1.0339	32.59
0.800	239.898	239.900	0.9471	0.9314	0.8338	1.0027	1.0380	27.92
0.850	242.568	242.567	0.9465	0.9307	0.8763	1.0022	1.0407	22.64
0.900	245.223	245.218	0.9460	0.9301	0.9181	1.0018	1.0437	17.05
0.950	247.758	247.751	0.9454	0.9295	0.9589	1.0008	1.0588	10.33
1.000	250.025	250.025	0.9449	0.9289	1.0000	1.0000	1.0931	0.0

been systematically filling the gaps in that UNIFAC parameter table. This paper brings to forty-nine the systems covered, which is almost one-half of those originally classified as PTx systems. All of those data have been published in this journal. The first one—Maher and Smith (2)—describes the apparatus and techniques used, and defines the activity coefficients and standard states used.

When publishing VLE data, we have always presented and reduced the "raw" P vs. x_1 values, even when small errors in the measured P values caused the activity coefficient curves to assume strange shapes, usually by hooking at their ends. In this paper, we demonstrate how sensitive the shapes of the activity coefficient curves are to the P values, and show how those curves can be straightened by very small adjustments of the experimental P values. From this demonstration, the users of our data will see what should be done to obtain the best possible activity coefficient values for those systems where our published activity coefficient curves show unusual shapes.

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

compd	T, K	P, MPa	ω
benzene	562.160	4.898	0.2090
acetonitrile	548.000	4.833	0.3210
diethylamine	496.600	3.708	0.2990
ethyl acetate	523.200	3.830	0.3620
propylamine	497.000	4.742	0.2290

Table XIV. Comparison of the Barker and Mixon et al. Pressure Fits. Peng-Robinson Equation of State

	max % dev in P^a		rms for % dev^b	
temp, K	Barker	Mixon	Barker	Mixon
	Benzene(1) + Acetonitrile(2)			
298.16	0.144	0.070	0.067	0.045
348.03	0.444	0.050	0.181	0.024
397.86	0.863	0.150	0.460	0.059
	Diethylamine(1) + Ethylacetate(2)			
297.98	0.167	0.082	0.060	0.037
348.09	0.038	0.013	0.019	0.007
398.03	0.099	0.008	0.059	0.005
	Propylamine(1) + Diethylamine(2)			
297.97	0.063	0.007	0.026	0.003
347.96	0.032	0.005	0.013	0.002

$$^a\% \ dev = 100 \left[|P_{calcd} - P_{exptl}| / P_{exptl} \right]$$

$$^b rms \ for \ \% \ dev = \left[\Sigma^n (\% \ dev)^2 / n \right]^{\frac{1}{2}}$$

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 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 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 cells at the end of last isotherm.

Experimental Data

The experimental PTx data measured for the three systems are given 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 (3).

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 deviation pressure plot emphasizes the scatter in the data more than a P vs. x_1 plot but has the disadvantages of not making obvious the existence of an azeotrope if one exists.

All the three binaries reported in this paper showed positive deviation from Raoult's law at all temperatures. The benzene + acetonitrile system exhibited azeotropes at all the three isotherms. The other two binaries did not show any azeotropes at any temperature.

Reduced Data

The calculated y_i, γ_i, and G^E values are reported in Tables V-XII. Those values were obtained with the Mixon et al. data reduction method, using the Peng-Robinson equation of state (4) to estimate the vapor-phase fugacity coefficients. The "experimental" pressure values tabulated in Tables V-XII 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 4-6 for both the Mixon et al. and the Barker (5) data reduction methods. The Barker results shown used the five-constant Redlich-Kister G^E equation for all three binary systems. The points in the figures represent the evenly spaced

Table XV. Effect of the Calculation Method on γ_i^∞ Values for the Benzene (1) + Acetonitrile (2) System. Peng-Robinson Equation of State Used

	Accuracy of P fits max % dev/rmsd			Calculated γ_i^∞ values					
				Component 1			Component 2		
Calculation method	298.16K	348.03K	397.86K	298.16K	348.03K	397.86K	298.16K	348.03K	397.86K
Mixon et al.	0.0/0.0	0.0/0.0	0.1/0.0	3.282	2.743	2.323	3.501	2.998	2.752
Barker:									
absolute Van Laar	1.1/0.5	0.8/0.4	1.0/0.4	2.920	2.496	2.168	2.862	2.562	2.254
Wilson	0.9/0.4	0.7/0.3	0.9/0.3	3.004	2.552	2.190	2.944	2.598	2.282
NRTL	1.1/0.5	0.2/0.1	1.0/0.4	2.941	2.756	2.166	2.866	2.839	2.259
modified Margules	0.2/0.0	0.0/0.0	0.3/0.1	3.166	2.681	2.294	3.376	2.963	2.626
UNIQUAC	1.0/0.5	0.7/0.3	1.0/0.4	2.953	2.520	2.187	2.899	2.593	2.278
Redlich-Kister, three constants	0.4/0.1	0.2/0.0	0.5/0.3	3.253	2.744	2.341	3.188	2.808	2.465
Redlich-Kister, five constants	0.1/0.0	0.4/0.2	0.8/0.5	3.260	2.709	2.236	3.400	2.645	2.797
Gautreaux-Coates:									
splined fits				3.289	2.747	2.326	3.508	3.005	2.759
$P_D/x_1 x_2$ plots				3.135	2.654	2.263	3.200	2.763	2.531

Table XVI. Comparison of the Original Experimental and Adjusted Pressures for the Propylamine (1) + Diethylamine (2) System

	297.97 K				347.96 K		
	P, kPa				P, kPa		
x_1	Experimental	Adjusted	ΔP^a, kPa	x_1	Experimental	Adjusted	ΔP^a, kPa
0.0	31.41	31.41	0.0	0.0	188.89	188.89	0.0
0.0355	31.88	31.88	0.0	0.0354	191.58	191.54	-0.04
0.0627	32.24	32.24	0.0	0.0626	193.60	193.60	0.0
0.1356	33.18	33.18	0.0	0.1355	198.91	198.91	0.0
0.2033	34.03	34.03	0.0	0.2032	203.68	203.68	0.0
0.2937	35.11	35.11	0.0	0.2936	209.81	209.81	0.0
0.3983	36.31	36.31	0.0	0.3981	216.56	216.59	0.03
0.4951	37.37	37.37	0.0	0.4947	222.57	222.57	0.0
0.6017	38.47	38.47	0.0	0.6015	228.91	228.90	-0.01
0.6979	39.41	39.45	0.04	0.6978	234.35	234.35	0.0
0.7892	40.27	40.29	0.02	0.7891	239.32	239.39	0.07
0.8578	40.91	40.95	0.04	0.8577	242.98	243.00	0.02
0.9187	41.49	41.49	0.0	0.9186	246.18	246.15	-0.03
0.9578	41.84	41.81	-0.03	0.9578	248.14	248.13	-0.01
1.0000	42.17	42.17	0.0	1.0000	250.02	250.02	0.0

$^a \Delta P$ = (Adjusted - Original) pressures

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 XIII 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 generally well-behaved. There are no mixed deviations and the level of nonideality changes monotonically with temperature in all cases. Therefore, the disagreements between different data reduction procedures are not as sharp as for less well-behaved systems. The disagreements were highest for the system benzene (1) + acetonitrile (2).

Table XIV compares the two data reduction methods in terms of accuracy of the pressure fits. The maximum percent deviation and the root-mean-squared deviation are defined at the bottom of the table. It is obvious from the table that the Mixon et al. data reduction method performs much better than the Barker method for every system at all temperatures.

A further comparison of the two data reduction methods is shown in Table XV in terms of infinite dilution activity coefficients obtained for the benzene (1) + acetonitrile (2) system. Table XV also shows the values obtained using the Gautreaux-Coates equations (6) when the $(dP/dx_1)^\infty$ values needed by those equations come from the cubic splined fits or from the $P_D/x_1 x_2$ or $x_1 x_2/P_D$ plots. The estimation of $\gamma_i{}^\infty$ values from the plots has been discussed before (7).

In the choice of the better data reduction method, the most weight must be given to how well the various procedures reproduce the experimental P vs. x_1 isotherm. Of the various G^E correlations used in the indirect Barker method the five-constant Redlich-Kister equation almost invariably gives the smallest pressure deviations with the five-constant modified Margules equation of Abbott and Van Ness (8) usually a close second. However, in the case of the benzene (1) + acetonitrile (2) system the modified Margules performed better than the five-constant Redlich-Kister equation. No restrictions were placed on the α in the NRTL equation; it was used as a three-constant equation.

The activity coefficient is a slope property and, when the total pressure method is used, the shape of the P vs. x_1 isotherm must be determined very accurately if reasonably shaped activity coefficient curves are to be obtained by the Mixon et al.

method. Figure 6 shows the activity coefficient values calculated from the raw P vs. x_1 values reported in Table IV for the propylamine + diethylamine binary. By trial and error, those raw values were adjusted slightly—as shown in Table XVI—to give the activity coefficient values shown in Figure 7. One point was adjusted by 0.07 kPa (0.53 mmHg)—a 0.03% change in the raw pressure value of 239.32 kPa. For all the other points changed, the adjustment was 0.04 kPa or less. For the lower temperature isotherm, 0.04 kPa is about 0.1% of the raw pressure value.

The Barker method is less sensitive to the slope of the P vs. x_1 isotherm at any given point. As shown by Figure 6, the Barker curves were reasonable for the raw P vs. x_1 data, and changed only slightly when the data were smoothed.

In all the past PTx VLE data published by the Thermodynamics Research Laboratory, we have always published only the raw P vs. x_1 values—none of the sets have ever been smoothed as done here in the propylamine + diethylamine example. Consequently, some of the published calculated activity coefficient curves have exhibited abnormalities in their shapes due to a small amount of scatter in the raw P values. The propylamine + diethylamine example presented here shows the user of those data sets what must be done to give normally shaped curves.

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