Phase Equilibrium Measurements on Twelve Binary Mixtures

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Phase equilibrium measurements have been performed on twelve binary mixtures. The *PTx* method was used to obtain vapor−liquid equilibrium data for the following binary systems at two temperatures each: ethanethiol + propylene; nitrobenzene + methanol; pyridine + ethyl acetate; octane + *tert*-amyl methyl ether; diisopropyl ether + butane; 1,3-dichloro-2-propanol + epichlorohydrin; 2,3-dichloro-1-propanol + epichlorohydrin; 2,3-epoxy-1-propanol + epichlorohydrin; 3-chloro-1,2-propanediol + epichlorohydrin; methanol + hydrogen cyanide. For these systems, equilibrium vapor and liquid phase compositions were derived from the *PTx* data using the Soave equation of state to represent the vapor phase and the Wilson, NRTL, or Redlich−Kister activity coefficient model to represent the liquid phase. The infinite dilution activity coefficient of methylamine in *N*-methyl-2-pyrrolidone was determined at three temperatures by performing *PTx* measurements on the *N*-methyl-2-pyrrolidone-rich half of the binary. Liquid−liquid equilibrium studies were made on the triethylene glycol + 1-pentene system at two temperatures by directly analyzing samples taken from each liquid phase.

Introduction

This work is part of an ongoing investigation of the phase equilibrium for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Property Data, DIPPR, of the American Institute of Chemical Engineers. This paper reports experimental measurements that have been made under Project 805/92 to obtain phase equilibrium data on twelve binary systems. These systems and their measurement conditions follow:

1. ethanethiol + propylene at −20 and 50 °C
2. nitrobenzene + methanol at 50.3 and 150 °C
3. pyridine + ethyl acetate at 50.3 and 150 °C
4. octane + *tert*-amyl methyl ether at 50 and 150 °C
5. diisopropyl ether + butane at 0 and 100 °C
6. 1,3-dichloro-2-propanol + epichlorohydrin at 50 and 100 °C
7. 2,3-dichloro-1-propanol + epichlorohydrin at 50 and 100 °C
8. 2,3-epoxy-1-propanol + epichlorohydrin at 50 and 75 °C
9. 3-chloro-1,2-propanediol + epichlorohydrin at 50 and 100 °C
10. methanol + hydrogen cyanide at 0 and 75 °C
11. *N*-methyl-2-pyrrolidone + methylamine at 50, 100, and 150 °C
12. triethylene glycol + 1-pentene at 0 and 100 °C

Vapor−liquid equilibrium data were determined for the first ten systems from total pressure−temperature−composition (*PTx*) measurements. With accurate pressure measurements and equations to model the vapor and liquid phases, *PTx* data can yield reliable phase composition information. An equation of state was used to represent the vapor phase, and an activity coefficient equation was used to represent the liquid phase. The infinite dilution activity coefficient of methylamine in *N*-methyl-2-pyrrolidone (NMP) was obtained from *PTx* measurements on the NMP-rich half of the binary. Liquid−liquid equilibrium data were obtained for the triethylene glycol + 1-pentene system by directly analyzing each liquid phase.

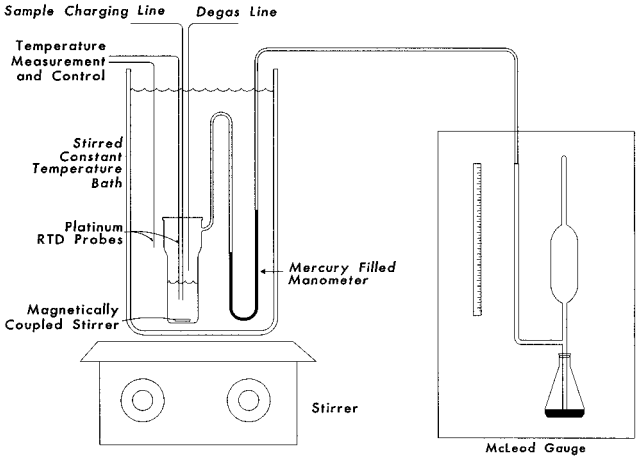

Figure 1. Glass *PTx* apparatus.

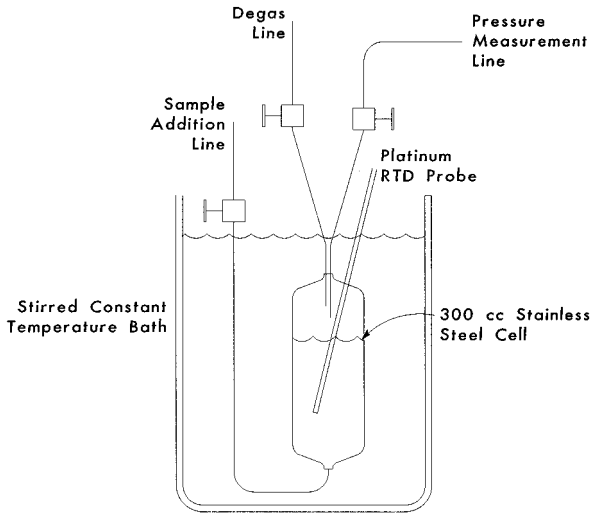

Figure 2. Stainless steel *PTx* apparatus.

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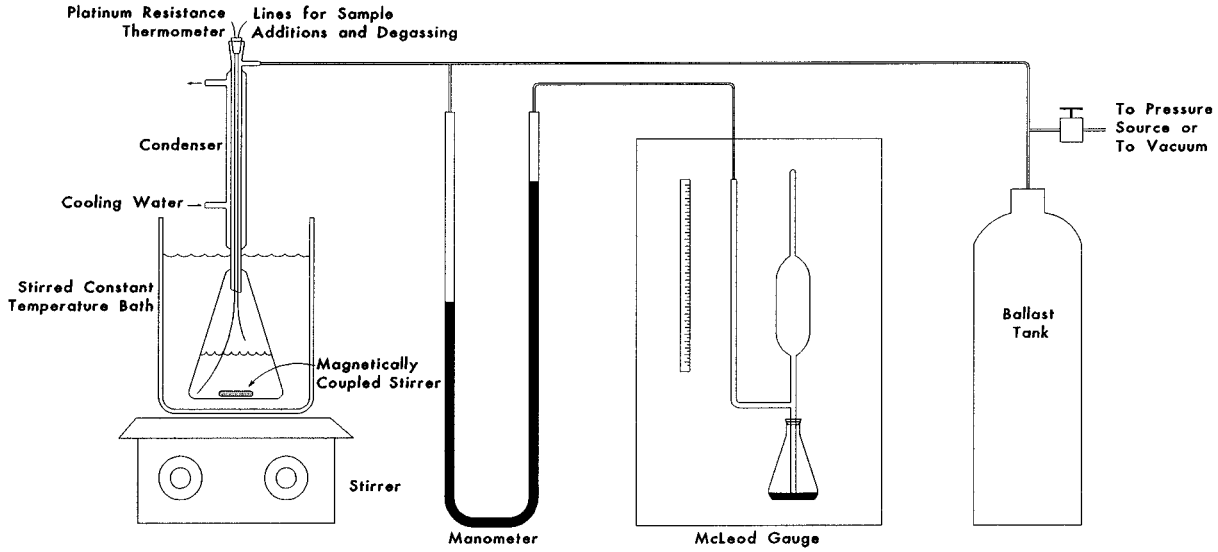

Figure 3. Glass still *PTx* apparatus.

Table 1. *PTx* Measurement Results for Ethanethiol (A) + Propylene (B)

				P/kPa								
run no.	$100z_A$	$100x_A$	$100y_A$	meas	calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = -20$ °C[a]							
1	100.00	100.00	100.00	8.810	8.810	1.000	1.896	0.9963	0.9984	1.000	0.9897	61.05
1	96.83	97.02	35.66	24.219	24.146	1.001	1.833	0.9901	0.9950	1.001	0.9902	58.83
1	94.61	94.93	24.62	34.444	34.399	1.001	1.791	0.9862	0.9927	1.001	0.9906	57.31
1	87.92	88.54	12.74	63.024	63.154	1.008	1.672	0.9750	0.9866	1.002	0.9916	52.91
1	79.88	80.72	8.03	93.503	93.875	1.022	1.545	0.9632	0.9800	1.003	0.9926	47.94
1	70.51	71.46	5.55	125.41	125.18	1.050	1.418	0.9512	0.9734	1.004	0.9937	42.58
1	58.51	59.38	3.87	159.94	159.86	1.107	1.284	0.9380	0.9660	1.005	0.9949	36.33
2	57.65	57.82	3.71	163.67	163.96	1.116	1.269	0.9364	0.9652	1.005	0.9951	35.58
1	48.67	49.36	2.98	185.13	185.04	1.176	1.195	0.9284	0.9607	1.006	0.9958	31.70
2	45.40	45.65	2.71	193.78	193.81	1.207	1.167	0.9251	0.9588	1.006	0.9961	30.11
2	36.80	37.09	2.17	213.65	213.43	1.294	1.111	0.9176	0.9547	1.007	0.9968	26.63
2	20.76	21.05	1.26	250.89	250.07	1.533	1.037	0.9038	0.9469	1.008	0.9981	20.84
2	11.15	11.35	0.72	274.82	274.00	1.747	1.011	0.8948	0.9418	1.009	0.9989	17.75
2	4.58	4.67	0.31	292.90	292.15	1.940	1.002	0.8881	0.9380	1.010	0.9995	15.78
2	1.64	1.67	0.11	300.83	300.94	2.042	1.000	0.8848	0.9361	1.010	0.9998	14.94
2	0.00	0.00	0.00	306.04	306.04	2.104	1.000	0.8829	0.9350	1.010	1.000	14.48
					$t = 50$ °C[b]							
1	100.00	100.00	100.00	165.65	165.65	1.000	1.725	0.9633	0.9858	1.0008	0.9369	15.96
1	96.83	97.31	70.11	235.47	234.03	1.000	1.680	0.9486	0.9775	1.002	0.9391	15.43
1	94.61	95.39	57.87	282.24	281.45	1.001	1.649	0.9387	0.9721	1.003	0.9407	15.07
1	87.92	89.39	37.61	421.51	422.16	1.006	1.558	0.9102	0.9565	1.007	0.9452	13.98
1	79.88	81.82	26.14	583.10	585.86	1.017	1.458	0.8778	0.9388	1.012	0.9506	12.72
1	70.51	72.56	18.94	768.70	768.02	1.040	1.352	0.8423	0.9194	1.018	0.9565	11.32
1	58.51	60.17	13.52	989.44	988.66	1.088	1.238	0.7999	0.8961	1.024	0.9638	9.662
2	57.65	58.19	12.88	1018.5	1022.2	1.097	1.222	0.7935	0.8926	1.025	0.9649	9.416
1	48.67	49.75	10.51	1164.7	1161.2	1.146	1.161	0.7672	0.8780	1.029	0.9696	8.430
2	45.40	46.38	9.69	1212.8	1215.7	1.169	1.140	0.7569	0.8722	1.031	0.9714	8.058
2	36.80	38.06	7.87	1352.9	1349.3	1.236	1.095	0.7318	0.8582	1.035	0.9759	7.194
2	20.76	22.16	4.74	1617.4	1613.5	1.416	1.033	0.6827	0.8304	1.043	0.9848	5.723
2	11.15	12.19	2.74	1802.0	1797.2	1.576	1.010	0.6489	0.8110	1.048	0.9910	4.901
2	4.58	5.10	1.22	1949.3	1942.9	1.719	1.002	0.6222	0.7956	1.053	0.9960	4.358
2	1.64	1.84	0.45	2013.5	2015.7	1.796	1.000	0.6089	0.7878	1.055	0.9985	4.118
2	0.00	0.00	0.00	2058.8	2058.8	1.843	1.000	0.6011	0.7832	1.056	1.000	3.985

[a] Wilson equation parameters: $\Lambda_{AB} = 0.5779$, $\Lambda_{BA} = 0.8044$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.6458$, $\Lambda_{BA} = 0.8260$.

Experimental Section

The measurements required to derive vapor and liquid compositions from *PTx* data are total pressure versus charge composition at constant temperature and known cell volume. In the *PTx* experiments, the entire composition range was traversed at a given temperature. Two or more runs were required for each isotherm. Where possible, the pure compounds comprising the binary were degassed prior to the start of a *PTx* run. To initiate a run, the cell was charged with a known amount of one component. The cell contents were degassed by withdrawing vapor into a weighed, evacuated cell or sample train in order to remove any air that may have been introduced to the cell upon charging as well as any light impurities that may have still been present in the chemicals. The cell contents were allowed to reach equilibrium at the desired temperature, and the pure component vapor pressure was measured. Further degassing was performed until a repeatable vapor pressure was obtained. Increments of the second component were then charged to the cell. After each increment,

Table 2. *PTx* Measurement Results for Nitrobenzene (A) + Methanol (B)

				P/kPa								
run no.	$100z_A$	$100x_A$	$100y_A$	meas	calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = 50.3$ °C							
1	100.00	100.00	100.00	0.203	0.203	1.000	7.363	0.9998	1.0000	1.000	0.9991	2025
1	95.70	95.80	1.39	14.235	14.124	1.005	5.933	0.9911	0.9972	1.001	0.9993	1614
1	93.21	93.35	0.97	19.897	19.913	1.011	5.294	0.9875	0.9961	1.001	0.9994	1427
1	90.00	90.17	0.74	25.521	25.658	1.024	4.622	0.9839	0.9949	1.001	0.9995	1228
1	81.39	81.58	0.52	35.085	35.198	1.077	3.384	0.9780	0.9931	1.001	0.9997	850.6
1	66.65	66.79	0.41	42.217	42.505	1.237	2.266	0.9735	0.9916	1.002	0.9998	494.5
2	60.22	60.26	0.38	44.186	44.249	1.339	1.971	0.9724	0.9913	1.002	0.9998	396.8
1	56.45	56.55	0.37	44.995	45.041	1.410	1.835	0.9719	0.9911	1.002	0.9998	350.9
2	50.39	50.46	0.35	46.140	46.127	1.548	1.648	0.9713	0.9909	1.002	0.9998	286.8
1	49.79	49.87	0.35	46.255	46.220	1.563	1.632	0.9712	0.9909	1.002	0.9998	281.3
2	40.13	40.21	0.33	47.717	47.576	1.871	1.408	0.9704	0.9906	1.002	0.9999	202.6
1	39.60	39.64	0.33	47.859	47.649	1.894	1.397	0.9703	0.9906	1.002	0.9999	198.6
2	30.04	30.11	0.31	49.111	48.829	2.381	1.237	0.9696	0.9904	1.002	0.9999	139.7
2	20.16	20.22	0.27	50.569	50.229	3.251	1.114	0.9688	0.9901	1.002	0.9999	92.15
2	10.13	10.16	0.20	52.608	52.386	5.012	1.032	0.9674	0.9897	1.002	0.9999	55.32
2	6.34	6.36	0.15	53.700	53.587	6.160	1.013	0.9667	0.9895	1.002	1.000	44.17
2	3.36	3.37	0.10	54.881	54.766	7.401	1.004	0.9660	0.9892	1.002	1.000	36.40
2	0.00	0.00	0.00	56.421	56.421	9.348	1.000	0.9650	0.9889	1.002	1.000	28.68
					$t = 150$ °C							
1	100.00	100.00	100.00	18.856	18.856	1.000	3.261	0.9921	1.001	1.000	0.9793	210.9
1	96.30	96.99	14.30	127.00	131.82	1.001	3.038	0.9580	0.9893	1.004	0.9810	193.1
1	93.75	94.84	9.20	204.29	204.86	1.003	2.894	0.9374	0.9830	1.006	0.9820	181.2
1	89.42	91.04	5.89	324.27	319.92	1.009	2.667	0.9057	0.9733	1.010	0.9837	162.2
1	79.15	81.39	3.43	547.87	550.02	1.040	2.213	0.8441	0.9540	1.018	0.9871	123.2
1	69.32	71.54	2.60	715.86	719.89	1.094	1.877	0.8001	0.9397	1.023	0.9897	94.12
1	60.83	62.75	2.18	833.02	834.83	1.165	1.650	0.7712	0.9301	1.027	0.9914	75.50
2	58.55	61.67	2.14	835.06	847.16	1.176	1.626	0.7681	0.9291	1.028	0.9915	73.51
2	49.42	53.10	1.87	929.86	934.85	1.275	1.457	0.7465	0.9218	1.031	0.9929	59.38
1	49.22	50.52	1.80	961.68	958.31	1.312	1.413	0.7408	0.9198	1.031	0.9932	55.64
2	38.16	42.17	1.60	1032.1	1027.6	1.459	1.290	0.7240	0.9141	1.034	0.9942	44.87
1	39.32	40.09	1.55	1049.7	1043.7	1.503	1.263	0.7202	0.9127	1.034	0.9945	42.46
2	29.73	33.50	1.40	1103.5	1093.1	1.672	1.187	0.7085	0.9086	1.036	0.9952	35.43
2	22.17	25.33	1.20	1166.1	1153.9	1.961	1.111	0.6943	0.9035	1.038	0.9961	27.84
2	10.54	12.46	0.79	1273.0	1262.8	2.733	1.030	0.6695	0.8944	1.042	0.9977	17.99
2	5.60	6.70	0.50	1331.9	1324.1	3.309	1.009	0.6560	0.8893	1.044	0.9987	14.34
2	2.74	3.29	0.27	1375.2	1366.5	3.765	1.002	0.6469	0.8858	1.045	0.9993	12.38
2	0.00	0.00	0.00	1413.1	1413.1	4.318	1.000	0.6371	0.8819	1.047	1.000	10.65

[a] NRTL parameters: $\tau_{AB} = 0.7491$, $\tau_{BA} = 0.6507$, $\alpha = -1.0000$. [b] NRTL parameters: $\tau_{AB} = 0.5903$, $\tau_{BA} = 0.3976$, $\alpha = -1.0000$.

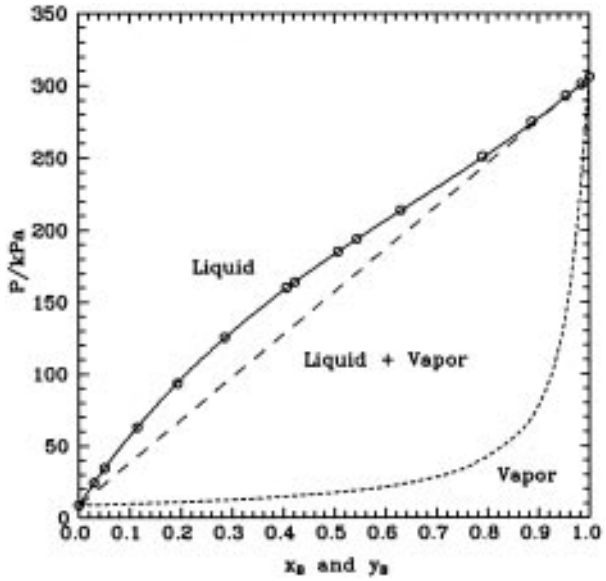

Figure 4. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for ethanethiol (A) + propylene (B) at −20 °C.

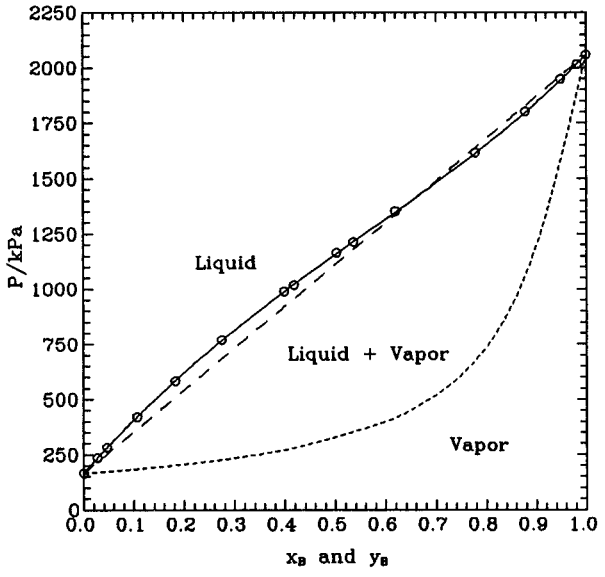

Figure 5. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for ethanethiol (A) + propylene (B) at 50 °C.

the cell contents were again degassed and allowed to equilibrate before the pressure was measured. The second and subsequent runs were similar to the first except that the second component was charged to the cell before adding increments of the first component. The ranges of compositions covered in the runs were designed to overlap to check for consistency between the runs.

Table 3. *PTx* Measurement Results for Pyridine (A) + Ethyl Acetate (B)

run no.	$100z_A$	$100x_A$	$100y_A$	P/kPa meas	P/kPa calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = 50.3$ °C							
1	100.00	100.00	100.00	9.773	9.773	1.000	1.206	0.9961	0.9962	1.000	0.9989	4.691
1	97.09	97.11	87.86	10.816	10.808	1.000	1.193	0.9957	0.9957	1.000	0.9990	4.637
1	94.45	94.48	78.85	11.746	11.727	1.001	1.181	0.9954	0.9954	1.000	0.9990	4.589
1	89.97	90.01	66.64	13.238	13.244	1.002	1.162	0.9948	0.9948	1.000	0.9990	4.509
1	80.13	80.19	48.25	16.379	16.411	1.008	1.124	0.9935	0.9935	1.000	0.9992	4.340
1	71.11	71.17	37.06	19.165	19.148	1.016	1.096	0.9924	0.9925	1.000	0.9993	4.193
1	60.12	60.17	27.29	22.353	22.324	1.031	1.066	0.9912	0.9912	1.000	0.9994	4.025
2	57.33	57.35	25.24	23.105	23.116	1.035	1.060	0.9909	0.9909	1.000	0.9994	3.983
2	54.29	54.31	23.18	23.969	23.959	1.040	1.053	0.9905	0.9906	1.000	0.9995	3.939
1	51.46	51.51	21.41	24.695	24.729	1.045	1.048	0.9902	0.9903	1.000	0.9995	3.899
2	44.91	44.93	17.65	26.510	26.515	1.058	1.036	0.9895	0.9896	1.001	0.9995	3.808
1	43.07	43.10	16.68	26.999	27.008	1.062	1.033	0.9893	0.9894	1.001	0.9996	3.783
2	34.64	34.67	12.63	29.250	29.259	1.081	1.021	0.9884	0.9885	1.001	0.9997	3.672
2	23.51	23.54	8.02	32.232	32.203	1.111	1.009	0.9873	0.9873	1.001	0.9998	3.532
2	13.67	13.69	4.44	34.853	34.811	1.142	1.003	0.9862	0.9863	1.001	0.9999	3.416
2	7.15	7.16	2.26	36.614	36.553	1.165	1.001	0.9855	0.9856	1.001	0.9999	3.342
2	3.22	3.22	1.00	37.672	37.611	1.179	1.000	0.9851	0.9852	1.001	1.000	3.298
2	0.00	0.00	0.00	38.484	38.484	1.192	1.000	0.9848	0.9849	1.001	1.000	3.263
					$t = 150$ °C							
1	100.00	100.00	100.00	251.74	251.74	1.000	1.197	0.9518	0.9555	1.000	0.9849	2.991
1	97.21	97.35	92.54	263.26	265.70	1.000	1.185	0.9492	0.9530	1.000	0.9854	2.961
1	94.61	94.86	86.29	277.50	278.57	1.000	1.175	0.9467	0.9507	1.001	0.9858	2.933
1	89.66	90.09	75.94	299.86	302.69	1.002	1.155	0.9421	0.9465	1.001	0.9866	2.880
1	79.92	80.56	59.86	347.98	348.87	1.007	1.121	0.9333	0.9383	1.003	0.9882	2.779
1	70.98	71.68	48.48	389.99	389.94	1.015	1.094	0.9255	0.9311	1.004	0.9896	2.690
2	62.72	63.02	39.54	428.62	428.52	1.025	1.071	0.9181	0.9243	1.005	0.9909	2.606
1	60.28	60.90	37.59	438.11	437.77	1.028	1.066	0.9164	0.9227	1.005	0.9912	2.586
2	52.90	53.36	31.24	468.60	470.33	1.040	1.050	0.9102	0.9169	1.006	0.9923	2.517
1	49.48	49.95	28.63	485.55	484.86	1.046	1.043	0.9074	0.9144	1.006	0.9928	2.487
2	42.07	42.68	23.49	514.68	515.54	1.060	1.031	0.9016	0.9090	1.007	0.9939	2.424
1	39.31	39.58	21.46	530.26	528.51	1.067	1.027	0.8991	0.9067	1.007	0.9943	2.398
2	31.98	32.64	17.15	556.67	557.52	1.083	1.018	0.8936	0.9016	1.008	0.9953	2.341
2	20.16	20.75	10.43	607.48	607.19	1.116	1.007	0.8841	0.8929	1.010	0.9970	2.248
2	10.32	10.70	5.23	651.52	649.57	1.147	1.002	0.8760	0.8854	1.011	0.9984	2.173
2	5.21	5.43	2.62	673.88	672.10	1.166	1.000	0.8717	0.8815	1.011	0.9992	2.135
2	3.74	3.90	1.87	680.65	678.67	1.171	1.000	0.8704	0.8803	1.012	0.9994	2.124
2	0.00	0.00	0.00	695.54	695.54	1.186	1.000	0.8672	0.8773	1.012	1.000	2.097

[a] Wilson equation parameters: $\Lambda_{AB} = 0.9738$, $\Lambda_{BA} = 0.8510$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.9643$, $\Lambda_{BA} = 0.8657$.

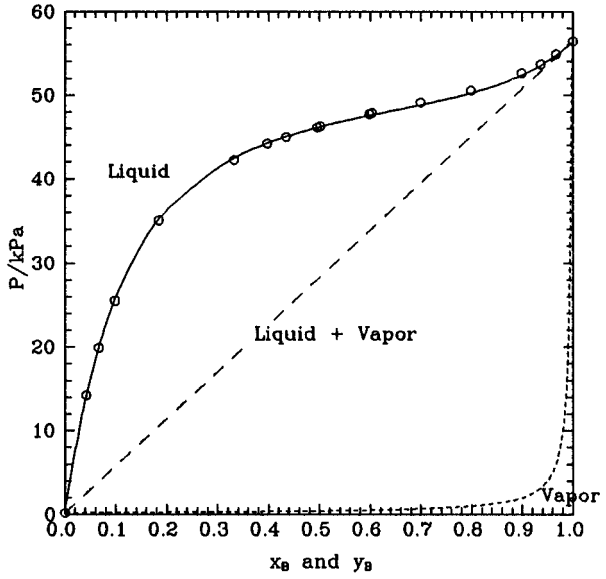

Figure 6. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for nitrobenzene (A) + methanol (B) at 50.3 °C.

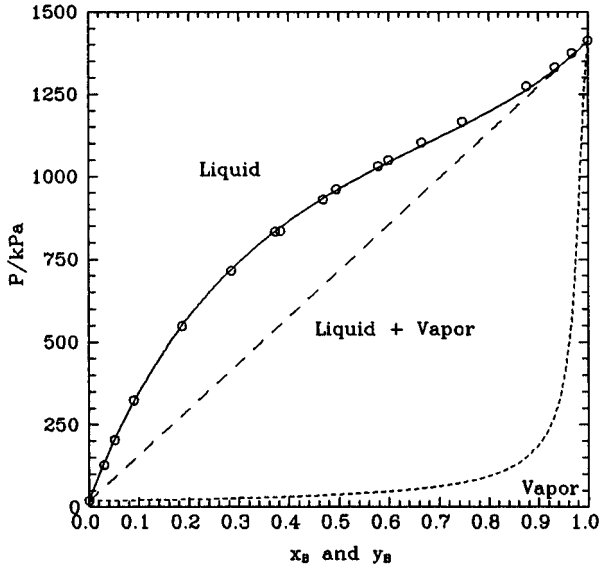

Figure 7. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for nitrobenzene (A) + methanol (B) at 150 °C.

Measurements were performed in the glass cell shown in Figure 1 at the lower temperatures for systems 2−4. The cell was made of thick-walled borosilicate glass with a TFE cap and had an internal volume of approximately 300 cm^3. The cap screwed into the cell and formed a seal with an O-ring. Small-bore lines through the cap were used for adding components and degassing. A thermowell into which a platinum resistance thermometer was inserted also extended into the cell.

The platinum thermometer was calibrated using ice and steam points and was referenced to a NIST traceable standard using the ITS-90 temperature scale. Tempera-

Table 4. *PTx* Measurement Results for Octane (A) + *tert*-Amyl Methyl Ether (B)

run no.	$100z_A$	$100x_A$	$100y_A$	P/kPa meas	P/kPa calc	γ_A	γ_B	ϕ_A	Λ_B	PF_A	PF_B	α_{BA}
					$t = 50$ °C[a]							
1	100.00	100.00	100.00	6.684	6.684	1.000	1.101	0.9947	0.9968	1.000	0.9988	4.764
1	97.16	97.17	87.85	7.369	7.397	1.000	1.099	0.9942	0.9964	1.000	0.9989	4.753
1	95.46	95.48	81.64	7.782	7.824	1.000	1.097	0.9938	0.9961	1.000	0.9989	4.746
1	90.66	90.69	67.35	8.947	9.021	1.000	1.093	0.9929	0.9955	1.000	0.9990	4.725
1	80.19	80.25	46.52	11.608	11.600	1.002	1.083	0.9909	0.9941	1.000	0.9991	4.671
1	70.23	70.30	33.93	14.092	14.004	1.005	1.072	0.9891	0.9929	1.000	0.9992	4.608
2	63.27	63.31	27.47	15.721	15.655	1.009	1.064	0.9879	0.9920	1.001	0.9993	4.555
1	60.94	61.00	25.64	16.209	16.196	1.011	1.062	0.9875	0.9917	1.001	0.9993	4.536
2	53.44	53.49	20.48	17.949	17.922	1.017	1.053	0.9862	0.9908	1.001	0.9994	4.466
1	50.99	51.03	19.00	18.429	18.480	1.020	1.050	0.9858	0.9905	1.001	0.9994	4.441
2	42.76	42.83	14.70	20.228	20.307	1.031	1.039	0.9844	0.9896	1.001	0.995	4.347
1	41.05	41.08	13.88	20.689	20.691	1.034	1.037	0.9841	0.9894	1.001	0.9996	4.325
2	32.42	32.50	10.28	22.606	22.542	1.053	1.027	0.9827	0.9884	1.001	0.9997	4.203
2	21.49	21.56	6.41	24.763	24.838	1.089	1.014	0.9810	0.9873	1.001	0.9998	4.011
2	11.34	11.39	3.28	26.822	26.933	1.142	1.005	0.9795	0.9862	1.001	0.9999	3.787
2	5.79	5.81	1.67	27.966	28.083	1.183	1.001	0.9787	0.9856	1.001	0.9999	3.643
2	3.68	3.69	1.06	28.450	28.524	1.202	1.001	0.9783	0.9854	1.001	1.000	3.583
2	0.00	0.00	0.00	29.300	29.300	1.239	1.000	0.9778	0.9850	1.001	1.000	3.472
					$t = 150$ °C[b]							
1	100.00	100.00	100.00	189.46	189.46	1.000	1.075	0.9316	0.9584	1.000	0.9856	2.578
1	96.18	96.33	91.08	201.32	201.44	1.000	1.072	0.9273	0.9552	1.001	0.9862	2.567
1	93.44	93.69	85.29	209.85	210.04	1.000	1.070	0.9243	0.9530	1.001	0.9866	2.559
1	90.23	90.57	79.04	219.25	220.15	1.000	1.067	0.9207	0.9504	1.002	0.9870	2.549
1	79.22	79.78	61.10	253.89	255.06	1.002	1.058	0.9086	0.9415	1.004	0.9886	2.512
1	69.24	69.86	48.37	285.88	286.84	1.005	1.049	0.8978	0.9336	1.005	0.9901	2.474
2	66.75	66.98	45.17	298.54	296.00	1.006	1.046	0.8947	0.9314	1.006	0.9905	2.462
1	59.35	59.91	38.07	319.24	318.33	1.010	1.040	0.8872	0.9259	1.007	0.9916	2.431
2	56.36	56.78	35.22	328.88	328.17	1.012	1.037	0.8840	0.9235	1.008	0.9920	2.417
1	47.97	48.38	28.30	354.13	354.36	1.018	1.029	0.8753	0.9172	1.009	0.9932	2.375
2	45.31	45.92	26.44	360.94	361.97	1.021	1.027	0.8728	0.9154	1.010	0.9936	2.362
1	38.64	38.89	21.50	385.53	383.59	1.029	1.021	0.8657	0.9102	1.011	0.9946	2.323
2	33.13	33.85	18.24	397.14	398.96	1.037	1.017	0.8607	0.9065	1.012	0.9953	2.293
2	22.32	22.98	11.84	430.10	431.76	1.058	1.009	0.8501	0.8987	1.013	0.9968	2.220
2	10.69	11.11	5.55	467.16	467.20	1.092	1.002	0.8388	0.8903	1.015	0.9985	2.128
2	5.41	5.64	2.79	483.79	483.51	1.113	1.001	0.8836	0.8865	1.016	0.9992	2.080
2	2.48	2.58	1.28	492.44	492.67	1.126	1.000	0.8308	0.8844	1.017	0.9996	2.052
2	0.00	0.00	0.00	500.41	1.139	1.000	0.8283	0.8825	1.017	1.000	2.027	

[a] Wilson equation parameters: $\Lambda_{AB} = 0.4655$, $\Lambda_{BA} = 1.5500$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.5784$, $\Lambda_{BA} = 1.4175$.

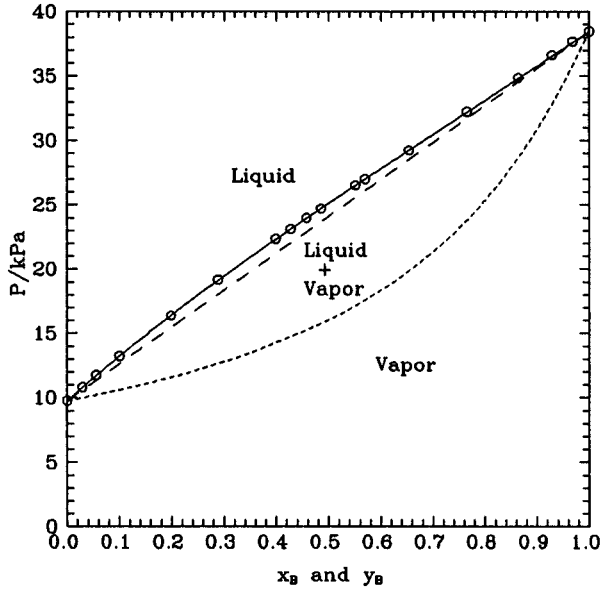

Figure 8. Measured *PTx* data (○), $P-x$ correlation (—), $P-y$ correlation (···), and Raoult's law (- - -) for pyridine (A) + ethyl acetate (B) at 50.3 °C.

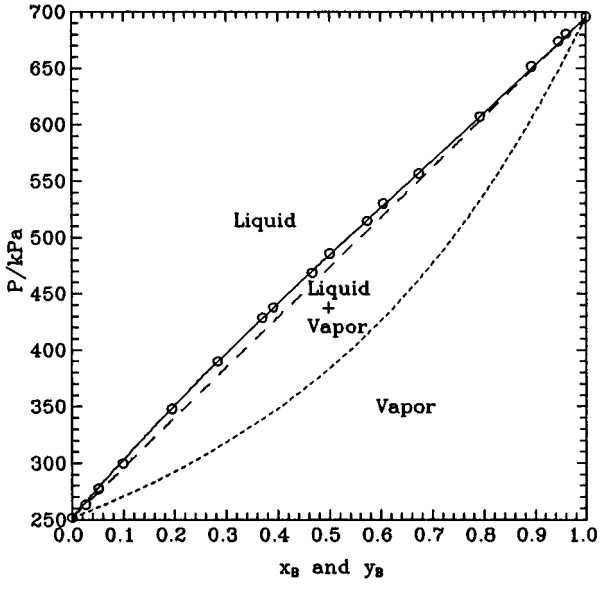

Figure 9. Measured *PTx* data (○), $P-x$ correlation (—), $P-y$ correlation (···), and Raoult's law (- - -) for pyridine (A) + ethyl acetate (B) at 150 °C.

tures in this and the other apparatuses were measured to an accuracy of ±0.05 deg or better.

The pressure was measured with the mercury manometer which extended from the side of the cell. The density and vapor pressure of the mercury at the bath temperature

Table 5. *PTx* Measurement Results for Diisopropyl Ether (A) + Butane (B)

run no.	$100z_A$	$100x_A$	$100y_A$	P/kPa meas	P/kPa calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = 0$ °C[a]							
1	100.00	100.00	100.00	5.757	5.757	1.000	1.128	0.9958	0.9986	1.000	0.9959	19.47
1	97.07	97.14	63.74	8.694	8.794	1.000	1.120	0.9936	0.9974	1.000	0.9960	19.32
1	91.39	91.58	36.38	14.623	14.600	1.001	1.106	0.9898	0.9954	1.001	0.9962	19.02
1	86.21	86.49	25.44	19.937	19.815	1.002	1.094	0.9864	0.9936	1.001	0.9965	18.76
1	78.73	79.09	17.07	27.202	27.243	1.005	1.078	0.9816	0.9911	1.001	0.9968	18.38
1	68.59	68.99	11.07	37.461	37.137	1.012	1.059	0.9752	0.9878	1.002	0.9972	17.88
2	58.78	59.16	7.68	45.986	46.577	1.020	1.043	0.9692	0.9847	1.002	0.9976	17.40
1	57.02	57.40	7.22	48.784	48.252	1.022	1.040	0.9681	0.9841	1.003	0.9977	17.32
2	48.59	49.07	5.39	55.317	56.127	1.032	1.029	0.9631	0.9816	1.003	0.9980	16.93
1	45.11	45.39	4.73	60.152	59.600	1.037	1.025	0.9609	0.9804	1.003	0.9981	16.76
2	39.94	40.46	3.95	63.616	64.241	1.044	1.020	0.9579	0.9789	1.004	0.9983	16.54
1	39.60	39.84	3.86	65.540	64.828	1.045	1.019	0.9575	0.9787	1.004	0.9984	16.51
2	29.78	30.30	2.63	73.350	73.815	1.060	1.011	0.9519	0.9757	1.004	0.9988	16.09
2	19.94	20.39	1.61	83.107	83.240	1.079	1.005	0.9459	0.9726	1.005	0.9992	15.66
2	10.97	11.28	0.83	92.164	92.022	1.099	0.002	0.9403	0.9698	1.005	0.9995	15.27
2	5.30	5.47	0.38	97.933	97.711	1.113	1.000	0.9368	0.9679	1.006	0.9998	15.03
2	2.09	2.16	0.15	101.20	100.98	1.121	1.000	0.9347	0.9668	1.006	0.9999	14.90
2	0.00	0.00	0.00	103.14	103.14	1.127	1.000	0.9334	0.9661	1.006	1.000	14.81
					$t = 100$ °C[b]							
1	100.00	100.00	100.00	250.07	250.07	1.000	1.043	0.9245	0.9763	1.000	0.9497	4.944
1	97.07	97.43	88.53	277.50	278.12	1.000	1.041	0.9162	0.9713	1.001	0.9508	4.913
1	91.39	92.35	71.34	335.11	333.92	1.000	1.036	0.9004	0.9620	1.004	0.9529	4.851
1	86.21	87.61	59.60	389.31	386.54	1.001	1.033	0.8860	0.9537	1.007	0.9550	4.793
1	78.73	80.55	46.81	468.60	465.82	1.002	1.028	0.8651	0.9418	1.011	0.9580	4.706
1	68.59	70.64	34.42	586.49	579.49	1.004	1.021	0.8360	0.9254	1.017	0.9624	4.584
2	58.78	60.69	25.71	691.34	696.78	1.006	1.016	0.8067	0.9089	1.023	0.9670	4.461
1	57.02	58.90	24.40	727.38	718.35	1.007	1.015	0.8014	0.9059	1.025	0.9678	4.439
2	48.59	51.25	19.49	797.81	811.77	1.010	1.011	0.7787	0.8930	1.030	0.9715	4.342
1	45.11	46.44	16.84	881.78	871.85	1.012	1.009	0.7643	0.8848	1.033	0.9738	4.281
2	39.94	42.96	15.10	903.45	915.98	1.014	1.008	0.7537	0.8788	1.035	0.9755	4.236
1	39.60	40.61	13.99	956.25	946.20	1.015	1.007	0.7465	0.8747	1.037	0.9767	4.206
2	29.78	33.07	10.74	1032.1	1045.4	1.019	1.005	0.7232	0.8613	1.042	0.9806	4.107
2	19.94	22.98	6.99	1172.9	1183.7	1.025	1.002	0.6910	0.8426	1.050	0.9861	3.971
2	10.97	13.26	3.83	1320.4	1324.6	1.032	1.001	0.6587	0.8237	1.057	0.9917	3.835
2	5.30	6.62	1.86	1425.9	1425.8	1.037	1.000	0.6357	0.8101	1.063	0.9958	3.738
2	2.09	2.67	0.74	1490.9	1488.3	1.040	1.000	0.6216	0.8017	1.066	0.9983	3.679
2	0.00	0.00	0.00	1531.5	1531.5	1.043	1.000	0.6119	0.7959	1.069	1.000	3.638

[a] Wilson equation parameters: $\Lambda_{AB} = 0.9472$, $\Lambda_{BA} = 0.9345$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.9811$, $\Lambda_{BA} = 0.9773$.

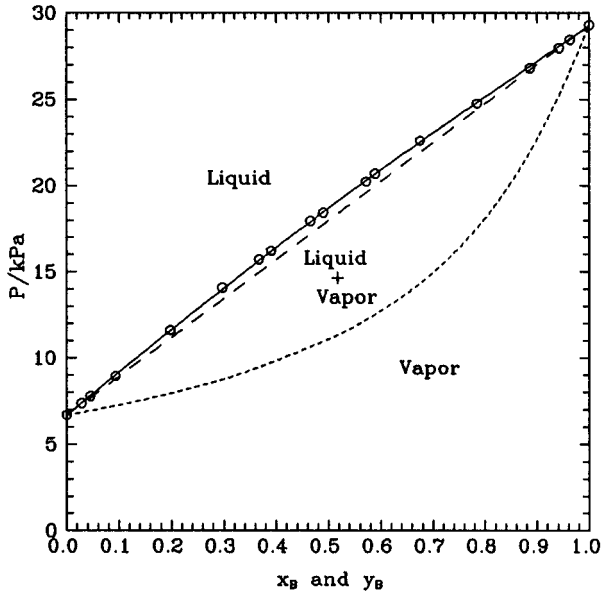

Figure 10. Measured *PTx* data (○), $P-x$ correlation (—), $P-y$ correlation (···), and Raoult's law (- - -) for octane (A) + *tert*-amyl methyl ether (B) at 50 °C.

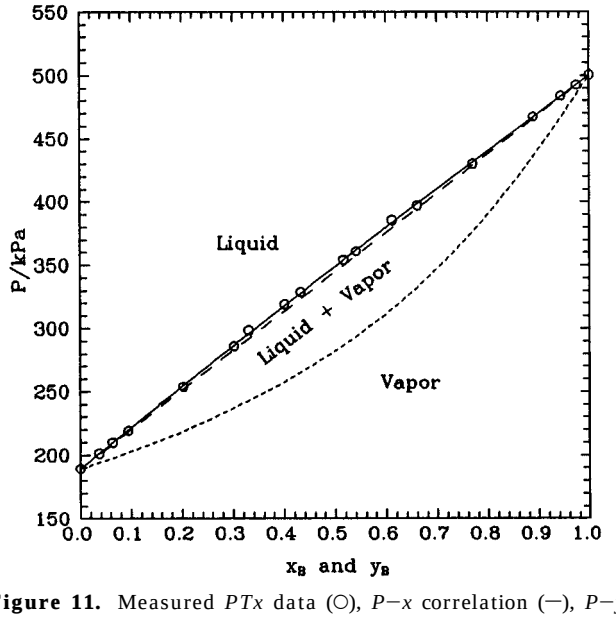

Figure 11. Measured *PTx* data (○), $P-x$ correlation (—), $P-y$ correlation (···), and Raoult's law (- - -) for octane (A) + *tert*-amyl methyl ether (B) at 150 °C.

were properly accounted for in the pressure determinations. The manometer was connected to a McLeod gauge for cell pressures below about 50 kPa or was left open to the atmosphere for higher pressures. Atmospheric pressure was measured with a barometer. The mercury levels in the cell manometer were read with a cathetometer to ±0.05 mm. Pressures measured with this apparatus are estimated to be accurate to ±0.05 kPa.

Systems 1, 5, 10, and 11 as well as the higher isotherms of systems 2−4 were studied in the stainless steel cell

Table 6. *PTx* Measurement Results for 1,3-Dichloro-2-propanol (A) + Epichlorohydrin (B)

				P/kPa								
run no.	$100z_A$	$100x_A$	$100y_A$	meas	calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
						$t = 50$ °C[a]						
1	100.00	100.00	100.00	0.584	0.584	1.000	0.7702	0.9996	0.9998	1.000	0.9998	11.05
1	95.38	95.38	64.00	0.865	0.870	0.9989	0.8095	0.9994	0.9996	1.000	0.9998	11.62
1	90.02	90.04	42.50	1.221	1.232	0.9952	0.8484	0.9992	0.9995	1.000	0.9998	12.22
1	79.99	80.01	23.30	1.970	1.976	0.9843	0.9045	0.9987	0.9991	1.000	0.9998	13.18
1	69.99	70.02	14.37	2.799	2.768	0.9710	0.9427	0.9981	0.9988	1.000	0.9998	13.92
2	59.91	59.92	9.35	3.560	3.590	0.9574	0.9679	0.9976	0.9984	1.000	0.9999	14.49
1	59.50	59.53	9.21	3.667	3.622	0.9569	0.9687	0.9976	0.9984	1.000	0.9999	14.51
2	50.35	50.37	6.38	4.369	4.373	0.9457	0.9829	0.9971	0.9981	1.000	0.9999	14.89
1	49.11	49.13	6.07	4.546	4.474	0.9443	0.9843	0.9970	0.9980	1.000	0.9999	14.94
2	39.31	39.33	4.08	5.284	5.272	0.9343	0.9928	0.9965	0.9977	1.000	0.9999	15.22
2	29.87	29.89	2.69	6.008	6.035	0.9267	0.9971	0.9959	0.9973	1.000	0.9999	15.41
2	19.86	19.88	1.57	6.837	6.834	0.9210	0.9992	0.9954	0.9970	1.000	1.000	15.54
2	10.05	10.06	0.71	7.666	7.613	0.9176	0.9999	0.9949	0.9966	1.000	1.000	15.60
2	4.80	4.81	0.32	8.037	8.029	0.9167	1.000	0.9946	0.9964	1.0000	1.000	15.62
2	0.00	0.00	0.00	8.409	8.409	0.9165	1.000	0.9944	0.9963	1.000	1.000	15.62
						$t = 100$ °C[b]						
1	100.00	100.00	100.00	7.926	7.926	1.000	0.8328	0.9964	0.9977	1.000	0.9985	6.304
1	97.04	97.06	83.71	9.107	9.193	0.9997	0.8491	0.9958	0.9973	1.000	0.9986	6.428
1	92.82	92.86	66.36	11.058	11.092	0.9984	0.8703	0.9949	0.9967	1.000	0.9986	6.596
1	86.92	86.99	49.53	13.975	13.893	0.9952	0.8961	0.9937	0.9959	1.000	0.9987	6.811
1	77.12	77.22	32.25	18.902	18.833	0.9872	0.9300	0.9915	0.9944	1.000	0.9988	7.120
1	66.83	66.94	21.51	24.361	24.289	0.9769	0.9558	0.9891	0.9927	1.001	0.9990	7.389
2	59.99	60.09	16.64	27.859	28.013	0.9696	0.9685	0.9875	0.9916	1.001	0.9991	7.539
1	56.96	57.06	14.88	29.727	29.671	0.9664	0.9731	0.9867	0.9911	1.001	0.9991	7.599
2	49.17	49.30	11.17	33.745	33.945	0.9582	0.9826	0.9849	0.9898	1.001	0.9992	7.734
1	48.12	48.21	10.72	34.720	34.548	0.9570	0.9837	0.9846	0.9896	1.001	0.9993	7.751
2	40.50	40.65	8.02	38.559	38.724	0.9495	0.9900	0.9828	0.9883	1.001	0.9994	7.858
1	37.80	37.86	7.17	40.271	40.267	0.9468	0.9918	0.9821	0.9879	1.001	0.9994	7.893
2	30.06	30.22	5.15	44.392	44.488	0.9400	0.9955	0.9802	0.9866	1.001	0.9995	7.975
2	19.76	19.89	2.99	50.131	50.174	0.9319	0.9985	0.9777	0.9849	1.001	0.9997	8.061
2	9.49	9.57	1.29	55.947	55.836	0.9252	0.9997	0.9753	0.9832	1.002	0.9999	8.123
2	7.21	7.27	0.96	57.169	57.096	0.9240	0.9998	0.9747	0.9828	1.002	0.9999	8.133
2	3.08	3.11	0.39	59.504	59.375	0.9219	1.000	0.9737	0.9821	1.002	1.000	8.150
2	0.00	0.00	0.00	61.076	61.076	0.9204	1.000	0.9730	0.9816	1.002	1.000	8.161

[a] NRTL parameters: $\tau_{AB} = -0.5512$, $\tau_{BA} = 0.2304$, $\alpha = -1.0000$. [b] NRTL parameters: $\tau_{AB} = -0.4136$, $\tau_{BA} = 0.1906$, $\alpha = -1.0000$.

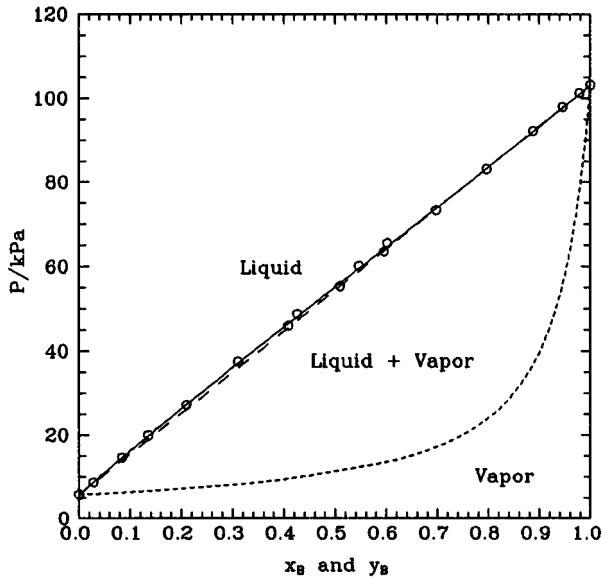

Figure 12. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for diisopropyl ether (A) + butane (B) at 0 °C.

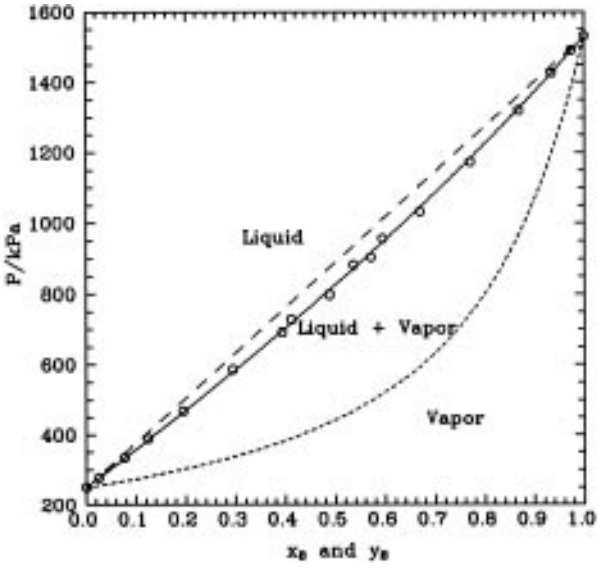

Figure 13. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for diisopropyl ether (A) + butane (B) at 100 °C.

shown in Figure 2. The cell had a volume of 300 cm^3 and was connected to external pressure gauges or manometers depending on the pressure range and run temperature. Lines were connected to the cell for charging, sampling, and degassing. A thermowell also extended into the cell into which a platinum resistance thermometer was inserted.

The cell and its connections were attached to a rigid support and immersed in a constant temperature bath. The cell was manually agitated to ensure the contents were at equilibrium at the desired temperature. Pressures less than about 200 kPa were measured with an external mercury manometer provided the run temperature was below room temperature. These pressure measurements were made with an estimated accuracy of ±0.05 kPa.

Table 7. *PTx* Measurement Results for 2,3-Dichloro-1-propanol (A) + Epichlorohydrin (B)

run no.	$100z_A$	$100x_A$	$100y_A$	P/kPa meas	P/kPa calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = 50$ °C[a]							
1	100.00	100.00	100.00	0.352	0.352	1.000	0.8246	0.9997	0.9999	1.000	0.9998	19.76
1	89.11	89.13	27.18	1.130	1.149	0.9945	0.9120	0.9992	0.9995	1.000	0.9998	21.98
1	79.63	79.66	14.23	1.945	1.941	0.9835	0.9695	0.9986	0.9991	1.000	0.9998	23.62
1	70.21	70.25	8.66	2.764	2.776	0.9707	1.009	0.9980	0.9988	1.000	0.9998	24.89
1	61.32	61.36	5.82	3.641	3.575	0.9600	1.031	0.9975	0.9984	1.000	0.9999	25.71
2	49.80	49.83	3.66	4.596	4.585	0.9529	1.041	0.9968	0.9980	1.000	0.9999	26.16
1	49.46	49.49	3.61	4.599	4.614	0.9529	1.041	0.9968	0.9980	1.000	0.9999	26.16
2	40.23	40.27	2.53	5.352	5.381	0.9568	1.038	0.9962	0.9976	1.000	0.9999	25.97
1	40.05	40.07	2.51	5.370	5.397	0.9570	1.038	0.9962	0.9976	1.000	0.9999	25.96
2	30.15	30.19	1.68	6.128	6.176	0.9747	1.028	0.9957	0.9973	1.000	0.9999	25.23
2	18.85	18.88	0.97	7.002	7.029	1.018	1.014	0.9951	0.9969	1.000	1.000	23.82
2	11.40	11.42	0.57	7.554	7.586	1.065	1.006	0.9947	0.9966	1.000	1.000	22.59
2	5.62	5.63	0.28	8.039	8.027	1.114	1.002	0.9944	0.9964	1.000	1.000	21.50
2	0.00	0.00	0.00	8.471	8.471	1.175	1.000	0.9941	0.9963	1.000	1.000	20.35
					$t = 100$ °C[b]							
1	100.00	100.00	100.00	5.353	5.353	1.000	0.9204	0.9974	0.9985	1.000	0.9984	10.31
1	90.16	90.30	46.45	10.027	10.413	0.9981	0.9565	0.9950	0.9969	1.000	0.9986	10.73
1	78.35	78.59	24.80	16.999	16.933	0.9924	0.9876	0.9920	0.9949	1.0008	0.9988	11.13
1	68.27	68.55	16.07	22.934	22.714	0.9865	1.004	0.9894	0.9932	1.001	0.9989	11.38
1	57.67	57.93	10.67	29.115	28.865	0.9814	1.014	0.9866	0.9913	1.001	0.9991	11.53
2	50.12	50.30	8.04	32.816	33.252	0.9795	1.016	0.9846	0.9900	1.001	0.9992	11.57
1	48.62	48.85	7.62	34.255	34.082	0.9794	1.016	0.9842	0.9897	1.001	0.9992	11.57
2	39.73	39.95	5.45	38.713	39.115	0.9809	1.015	0.9819	0.9882	1.001	0.9994	11.53
1	37.50	37.66	4.99	40.581	40.396	0.9820	1.014	0.9813	0.9878	1.001	0.9994	11.51
2	29.98	30.20	3.66	44.171	44.529	0.9880	1.011	0.9794	0.9866	1.001	0.9995	11.40
2	19.72	19.91	2.18	49.983	50.162	1.003	1.006	0.9769	0.9849	1.002	0.9997	11.15
2	9.55	9.67	0.98	55.785	55.751	1.029	1.002	0.9743	0.9832	1.002	0.9999	10.82
2	5.58	5.66	0.56	58.107	57.962	1.043	1.001	0.9733	0.9826	1.002	0.9999	10.66
2	0.00	0.00	0.00	61.119	61.119	1.066	1.000	0.9719	0.9816	1.002	1.000	10.42

[a] Redlich−Kister parameters: $A = -0.0158$, $B = -0.1770$, $C = 0.0$. [b] Redlich−Kister parameters: $A = -0.0096$, $B = -0.0734$, $C = 0.0$.

Table 8. *PTx* Measurement Results for 2,3-Epoxy-1-propanol (A) + Epichlorohydrin (B)

run no.	$100z_A$	$100x_A$	$100y_A$	P/kPa meas	P/kPa calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = 50$ °C[a]							
1	100.00	100.00	100.00	0.910	0.910	1.000	2.324	0.9995	0.9996	1.000	0.9998	21.46
1	88.93	88.97	30.40	2.624	2.688	1.008	2.016	0.9986	0.9988	1.000	0.9998	18.46
1	80.06	80.11	19.83	3.788	3.786	1.028	1.814	0.9980	0.9983	1.000	0.9999	16.29
1	69.12	69.17	13.96	4.852	4.844	1.072	1.606	0.9975	0.9979	1.000	0.9999	13.83
2	60.74	60.76	11.35	5.470	5.487	1.123	1.472	0.9971	0.9976	1.000	0.9999	12.10
1	59.47	59.51	11.04	5.592	5.573	1.133	1.454	0.9971	0.9975	1.000	0.9999	11.85
2	50.00	50.02	9.06	6.094	6.151	1.220	1.328	0.9968	0.9973	1.000	0.9999	10.05
1	49.33	49.36	8.94	6.213	6.187	1.228	1.321	0.9968	0.9973	1.000	0.9999	9.928
2	39.80	39.82	7.42	6.631	6.664	1.360	1.217	0.9965	0.9971	1.000	0.9999	8.260
1	38.92	38.94	7.29	6.726	6.705	1.375	1.208	0.9965	0.9970	1.000	0.9999	8.111
2	30.08	30.11	6.05	7.103	7.089	1.560	1.131	0.9963	0.9969	1.000	1.000	6.691
2	19.69	19.71	4.54	7.554	7.518	1.895	1.060	0.9961	0.9967	1.000	1.000	5.164
2	9.89	9.90	2.76	7.969	7.943	2.420	1.017	0.9959	0.9965	1.000	1.000	3.877
2	6.32	6.33	1.92	8.141	8.111	2.695	1.007	0.9958	0.9964	1.000	1.000	3.449
2	0.00	0.00	0.00	8.434	8.434	3.362	1.000	0.9956	0.9963	1.000	1.000	2.746
					$t = 75$ °C[b]							
1	100.00	100.00	100.00	3.512	3.512	1.000	2.305	0.9985	0.9987	1.000	0.9994	16.10
1	94.58	94.64	54.21	6.025	6.151	1.002	2.139	0.9974	0.9978	1.000	0.9995	14.91
1	89.45	89.55	38.22	8.386	8.311	1.008	2.000	0.9965	0.9970	1.000	0.9995	13.86
1	79.15	79.29	24.31	12.011	11.862	1.032	1.762	0.9950	0.9957	1.000	0.9996	11.92
1	68.42	68.55	17.71	14.823	14.705	1.077	1.562	0.9938	0.9947	1.000	0.9997	10.12
2	59.65	59.75	14.44	16.377	16.551	1.132	1.427	0.9930	0.9940	1.000	0.9998	8.797
1	58.69	58.80	14.15	16.759	16.730	1.140	1.414	0.9930	0.9939	1.000	0.9998	8.660
2	49.75	49.87	11.80	18.108	18.253	1.222	1.302	0.9923	0.9934	1.000	0.9998	7.436
1	46.67	46.74	11.10	18.754	18.729	1.258	1.267	0.9921	0.9932	1.000	0.9998	7.031
2	40.81	40.94	9.90	19.472	19.552	1.336	1.208	0.9918	0.9929	1.000	0.9999	6.310
2	30.46	30.57	7.92	20.872	20.882	1.529	1.121	0.9912	0.9924	1.000	0.9999	5.117
2	20.01	20.09	5.88	22.198	22.147	1.829	1.056	0.9907	0.9920	1.000	0.9999	4.029
2	12.33	12.38	4.10	23.186	23.091	2.160	1.023	0.9903	0.9916	1.000	1.000	3.303
2	7.41	7.44	2.72	23.843	23.723	2.449	1.009	0.9900	0.9914	1.000	1.000	2.873
2	0.00	0.00	0.00	24.733	24.733	3.064	1.000	0.9896	0.9910	1.001	1.000	2.277

[a] NRTL parameters: $\tau_{AB} = 0.5629$, $\tau_{BA} = 0.2241$, $\alpha = -1.0000$. [b] NRTL parameters: $\tau_{AB} = 0.5193$, $\tau_{BA} = 0.2467$, $\alpha = -1.0000$.

Table 9. *PTx* Measurement Results for 3-Chloro-1,2-propanediol (A) + Epichlorohydrin (B)

run no.	$100z_A$	$100x_A$	$100y_A$	P/kPa meas	P/kPa calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = 50$ °C[a]							
1	100.00	100.00	100.00	0.026	0.026	1.000	2.812	1.000	1.000	1.000	0.9997	918.3
1	87.99	88.05	0.96	2.419	2.413	1.011	2.365	0.9982	0.9989	1.000	0.9998	763.1
1	80.65	80.71	0.61	3.489	3.514	1.030	2.140	0.9973	0.9984	1.000	0.9999	677.7
1	69.91	69.97	0.41	4.781	4.755	1.078	1.863	0.9964	0.9979	1.000	0.9999	563.4
1	60.62	60.68	0.32	5.582	5.555	1.145	1.663	0.9958	0.9975	1.000	0.9999	473.2
2	50.35	50.40	0.27	6.235	6.218	1.261	1.476	0.9953	0.9972	1.000	0.9999	381.5
1	50.06	50.10	0.26	6.203	6.234	1.265	1.471	0.9953	0.9971	1.000	0.9999	379.0
2	40.17	40.22	0.22	6.686	6.706	1.442	1.321	0.9949	0.9970	1.000	0.9999	298.5
1	39.98	40.00	0.22	6.687	6.715	1.447	1.318	0.9949	0.9970	1.000	0.9999	296.8
2	29.95	30.00	0.19	7.091	7.092	1.743	1.193	0.9946	0.9969	1.000	1.000	223.1
2	19.64	19.67	0.16	7.495	7.448	2.284	1.092	0.9944	0.9967	1.000	1.000	155.8
2	9.37	9.38	0.10	7.875	7.874	3.360	1.024	0.9941	0.9965	1.000	1.000	99.28
2	4.44	4.45	0.06	8.162	8.153	4.284	1.006	0.9938	0.9964	1.000	1.000	76.47
2	0.00	0.00	0.00	8.479	8.479	5.568	1.000	0.9936	0.9962	1.000	1.000	58.49
					$t = 100$ °C							
1	100.00	100.00	100.00	0.726	0.726	1.000	2.317	0.996	0.9998	1.000	0.9983	191.4
1	90.82	91.05	5.65	11.544	11.818	1.005	2.073	0.9942	0.9964	1.000	0.9986	169.9
1	80.82	81.15	2.82	21.545	21.590	1.024	1.845	0.9894	0.9935	1.001	0.9989	148.2
1	69.72	70.07	1.82	30.995	30.134	1.066	1.634	0.9852	0.9909	1.001	0.9991	125.9
2	60.08	60.30	1.39	35.982	36.065	1.124	1.478	0.9823	0.9891	1.001	0.9993	107.8
1	59.62	59.92	1.38	36.717	36.272	1.127	1.472	0.9822	0.9891	1.001	0.9993	107.2
2	50.00	50.27	1.10	40.989	40.994	1.216	1.343	0.9799	0.9877	1.001	0.9994	90.53
1	49.74	49.97	1.10	40.947	41.125	1.219	1.339	0.9798	0.9876	1.001	0.9994	90.04
2	39.83	40.11	0.89	45.284	45.131	1.355	1.228	0.9778	0.9864	1.001	0.9996	74.26
1	39.39	39.53	0.88	44.818	45.348	1.364	1.223	0.9777	0.9863	1.001	0.9996	73.38
2	29.96	30.22	0.72	48.835	48.673	1.562	1.138	0.9761	0.9853	1.001	0.9997	59.62
2	19.83	20.04	0.54	52.258	52.207	1.901	1.066	0.9744	0.9843	1.002	0.9998	45.85
2	10.26	10.39	0.34	55.965	55.926	2.439	1.019	0.9726	0.9832	1.002	0.9999	34.16
2	4.74	4.81	0.18	58.445	58.498	2.923	1.004	0.9713	0.9824	1.002	0.9999	28.07
2	0.00	0.00	0.00	61.124	61.124	3.509	1.000	0.9700	0.9816	1.002	1.000	23.27

[a] NRTL parameters: $\tau_{AB} = 0.7173$, $\tau_{BA} = 0.2473$, $\alpha = -1.0000$. [b] NRTL parameters: $\tau_{AB} = 0.5840$, $\tau_{BA} = 0.2081$, $\alpha = -1.000$.

Table 10. Results of Vapor Pressure Measurements for 3-Chloro-1,2-propanediol

t/°C	P/kPa meas	P/kPa corr	% dev
70.58[a]	0.116	0.115	0.46
75.70[a]	0.161	0.163	−1.07
79.99[a]	0.217	0.215	0.84
84.46[a]	0.285	0.286	−0.28
101.37[b]	0.793	0.785	1.01
112.06[b]	1.416	1.418	−0.15
119.97[b]	2.098	2.150	−2.50
127.64[b]	3.166	3.168	−0.07
135.67[b]	4.764	4.678	1.81
213.00[c]	101.325	101.444	−0.12

$$\ln(P/\text{kPa}) = 20.4077 - 7485.96/(T/\text{K} - 12.0)$$

[a] Data measured in this work. [b] Data measured by Wilding and Wilson (1994). [c] Normal boiling point reported by Aldrich Chemical Co.

Higher pressures were measured using 3-D Instruments precision pressure gauges which were calibrated with a dead-weight piston gauge. These pressures were measured to within ±1 kPa for pressures up to 400 kPa and within ±0.25% for pressures above 400 kPa.

Measurements were performed in the glass still apparatus shown in Figure 3 for systems 6−9. This apparatus was also used to obtain the vapor pressure curve for 3-chloro-1,2-propanediol. The cell was connected to a large ballast tank and to a mercury or oil manometer. Lines through the top of the cell were for charging and degassing. A thermowell extended through the top of the cell into the liquid in the cell. The cell was placed in a constant temperature bath that was controlled at a temperature 2 deg warmer than the saturation temperature of the material in the cell to promote refluxing in the cell. The liquid in the cell was vigorously stirred to ensure good contact between the vapor and liquid phases and to prevent superheating in the liquid. The ballast tank pressure was used to control the cell temperature. This pressure was adjusted to obtain the desired temperature. Once equilibrium was established, the pressure and temperature were recorded. Pressures were measured with this apparatus with an estimated accuracy of ±0.025 kPa.

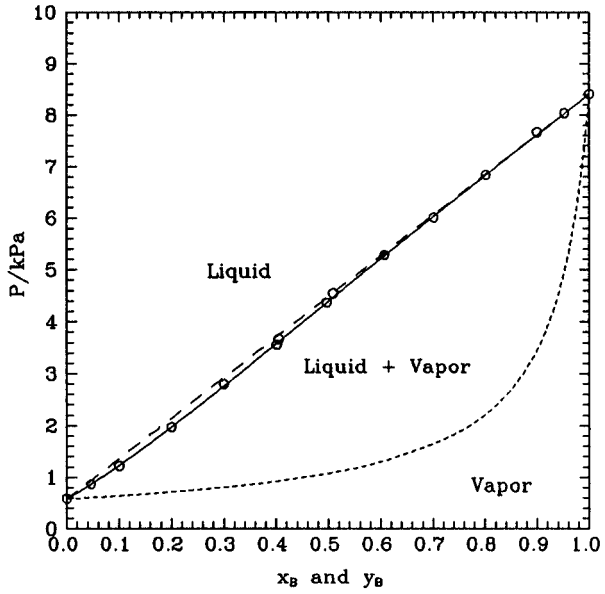

Figure 14. Measured *PTx* data (○), $P-x$ correlation (—), $P-y$ correlation (···), and Raoult's law (- - -) for 1,3-dichloro-2-propanol (A) + epichlorohydrin (B) at 50 °C.

Liquid−liquid equilibrium (LLE) data for system 12 were obtained by sampling and analyzing the equilibrium phases. At 0 °C the measurements were performed in a glass cell

Table 11. *PTx* Measurement Results for Methanol (A) + Hydrogen Cyanide (B)

run no.	$100z_A$	$100x_A$	$100y_A$	P/kPa meas	P/kPa calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = 0$ °C[a]							
1	100.00	100.00	100.00	4.009	4.009	1.000	0.7004	0.9987	0.9987	1.000	0.9995	6.089
1	95.14	95.15	74.40	5.109	5.117	0.9976	0.7742	0.9984	0.9984	1.000	0.9995	6.747
1	89.55	89.56	53.47	6.636	6.654	0.9900	0.8500	0.9979	0.9979	1.000	0.9995	7.465
1	82.55	82.57	36.43	8.925	8.885	0.9761	0.9284	0.9971	0.9972	1.000	0.9996	8.269
1	74.90	74.93	24.95	11.603	11.577	0.9591	0.9917	0.9963	0.9963	1.000	0.9996	8.988
1	65.90	65.92	16.80	14.819	14.863	0.9415	1.037	0.9952	0.9953	1.000	0.9997	9.579
1	58.00	58.02	12.30	17.620	17.697	0.9315	1.056	0.9943	0.9944	1.000	0.9997	9.854
2	49.73	49.74	9.08	20.596	20.522	0.9293	1.059	0.9934	0.9935	1.000	0.9998	9.908
1	47.94	47.96	8.52	21.034	21.107	0.9302	1.058	0.9932	0.9933	1.000	0.9998	9.891
2	39.60	39.62	6.34	23.871	23.730	0.9410	1.049	0.9924	0.9924	1.000	0.9998	9.691
2	25.74	25.76	3.70	27.744	27.777	0.9875	1.026	0.9911	0.9912	1.000	0.9999	9.028
2	16.98	17.00	2.36	30.202	30.247	1.037	1.012	0.9903	0.9904	1.000	0.9999	8.480
2	9.71	9.72	1.33	32.307	32.324	1.092	1.004	0.9896	0.9897	1.000	1.000	7.995
2	5.63	5.63	0.77	33.484	33.521	1.128	1.001	0.9892	0.9893	1.001	1.000	7.720
2	0.00	0.00	0.00	35.221	35.221	1.183	1.000	0.9887	0.9888	1.001	1.000	7.348
					$t = 75$ °C[b]							
1	100.00	100.00	100.00	150.51	150.51	1.000	0.8327	0.9763	0.9766	1.000	0.9948	2.515
2	95.14	95.18	88.18	163.06	162.62	0.9988	0.8755	0.9744	0.9747	1.000	0.9950	2.647
3	89.55	89.62	75.62	178.02	178.37	0.9950	0.9174	0.9719	0.9723	1.000	0.9953	2.785
4	82.55	82.66	61.93	200.29	200.24	0.9880	0.9588	0.9685	0.9689	1.001	0.9956	2.931
5	74.90	75.03	49.58	226.15	226.09	0.9794	0.9911	0.9644	0.9649	1.001	0.9960	3.056
6	65.90	66.03	38.12	257.73	257.85	0.9703	1.014	0.9594	0.9599	1.002	0.9965	3.156
7	58.00	58.12	30.23	285.99	286.03	0.9650	1.023	0.9550	0.9556	1.002	0.9969	3.202
15	49.73	49.78	23.58	315.85	315.34	0.9635	1.025	0.9504	0.9510	1.002	0.9974	3.214
8	47.94	48.01	22.34	320.95	321.49	0.9638	1.025	0.9494	0.9501	1.003	0.9975	3.211
14	39.60	39.69	17.13	350.39	350.02	0.9686	1.021	0.9450	0.9456	1.003	0.9979	3.183
13	25.74	25.85	10.15	396.86	396.23	0.9894	1.011	0.9377	0.9385	1.004	0.9987	3.085
12	16.98	17.08	6.42	424.23	425.16	1.011	1.005	0.9332	0.9340	1.004	0.9991	3.002
11	9.71	9.78	3.57	448.57	449.37	1.033	1.002	0.9293	0.9303	1.004	0.9995	2.927
10	5.63	5.67	2.04	462.84	463.14	1.047	1.001	0.9272	0.9281	1.005	0.9997	2.884
9	0.00	0.00	0.00	482.36	482.36	1.068	1.000	0.9242	0.9252	1.005	1.000	2.825

[a] Redlich−Kister parameters: $A = -0.0315$, $B = -0.2620$, $C = -0.0626$. [b] Redlich−Kister parameters: $A = -0.0243$, $B = -0.1246$, $C = -0.0342$.

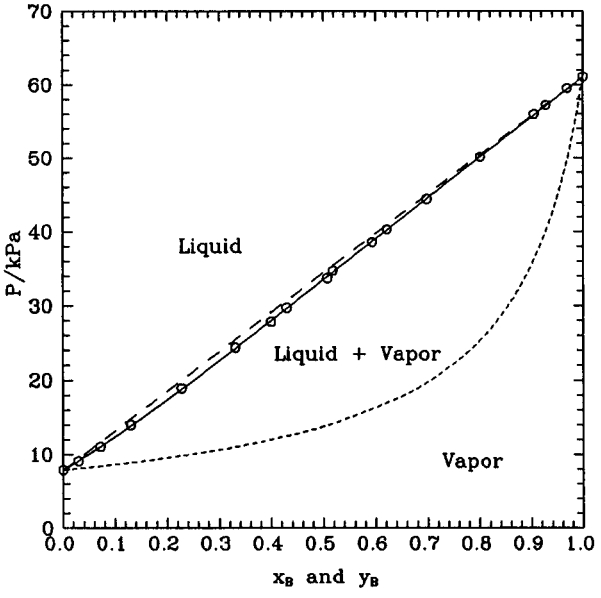

Figure 15. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 1,3-dichloro-2-propanol (A) + epichlorohydrin (B) at 100 °C.

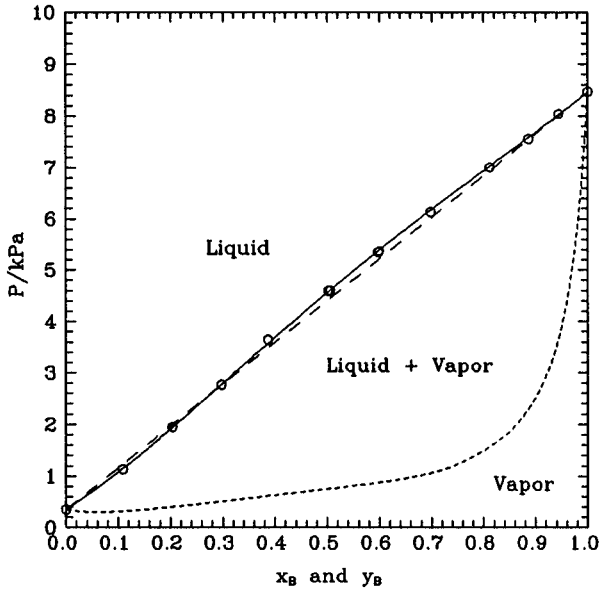

Figure 16. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2,3-dichloro-1-propanol (A) + epichlorohydrin (B) at 50 °C.

similar to that shown in Figure 1, except the cell was equipped with sample lines which extended through the Teflon cap into the two liquid phases. The glass cell was vigorously agitated by hand to ensure that the cell contents were well mixed. This was done because the lower liquid phase was so viscous at 0 °C that the magnetic stir bar was unable to adequately mix the two phases. The phases were allowed to settle before withdrawing multiple samples of both liquid phases into previously weighed sample trains.

The amount of TEG in a sample was determined by carefully heating the sample train to around 50 °C for about 1 min to drive off the 1-pentene. The train was then weighed and carefully heated again. This procedure was repeated until the mass of the sample train did not change. The amount of 1-pentene in the sample was obtained by difference. This procedure could be used without losing any of the TEG due to the difference in the vapor pressures of these two compounds. While the vapor pressures of TEG

Table 12. *PTx* Measurement Results for *N*-Methyl-2-pyrrolidone (A) + Methylamine (B)

run no.	$100z_A$	$100x_A$	$100y_A$	P/kPa meas	P/kPa calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = 50$ °C[a]							
1	100.00	100.00	100.00	0.249	0.249	1.000	1.021	0.9998	1.000	1.000	0.9855	2877
2	98.07	98.24	1.90	13.452	12.944	1.000	1.023	0.9938	0.9986	1.000	0.9858	2869
2	95.92	96.27	0.89	27.220	27.197	0.9999	1.025	0.9871	0.9970	1.001	0.9860	2860
2	93.73	94.25	0.57	41.520	41.978	0.9998	1.028	0.9802	0.9953	1.002	0.9863	2851
2	90.63	91.34	0.37	62.494	63.461	0.9996	1.031	0.9702	0.9929	1.002	0.9867	2837
1	84.73	85.10	0.20	111.42	110.38	0.9987	1.037	0.9486	0.9876	1.004	0.9876	2806
1	79.04	79.49	0.14	154.79	153.50	0.9977	1.042	0.9290	0.9828	1.006	0.9884	2777
1	70.01	70.50	0.09	227.32	224.23	0.9955	1.049	0.8974	0.9749	1.008	0.9897	2724
1	60.30	60.74	0.06	304.26	302.82	0.9933	1.054	0.8632	0.9661	1.011	0.9911	2658
1	48.31	48.61	0.04	400.17	401.98	0.9927	1.055	0.8210	0.9551	1.015	0.9930	2557
1	39.03	39.20	0.03	474.01	478.81	0.9974	1.051	0.7893	0.9465	1.018	0.9944	2456
					$t = 100$ °C[b]							
1	100.00	100.00	100.00	3.434	3.434	1.000	1.093	0.9982	1.000	1.000	0.9514	652.0
1	95.54	95.89	3.54	90.735	96.156	1.000	1.092	0.9685	0.9931	1.003	0.9531	635.8
1	92.04	92.63	1.98	170.37	170.79	1.000	1.091	0.9455	0.9876	1.006	0.9544	622.8
1	88.71	89.48	1.38	244.28	243.50	1.000	1.090	0.9234	0.9824	1.008	0.9557	610.1
1	84.73	85.68	1.00	333.77	332.41	1.000	1.088	0.8970	0.9760	1.011	0.9573	594.7
1	79.04	80.18	0.70	463.88	463.21	1.001	1.085	0.8589	0.9665	1.015	0.9596	572.1
1	69.57	70.81	0.45	686.72	691.21	1.003	1.079	0.7951	0.9502	1.023	0.9637	532.9
1	59.97	61.09	0.32	932.24	934.49	1.007	1.071	0.7304	0.9327	1.031	0.9682	491.1
1	48.10	48.83	0.22	1250.0	1249.9	1.017	1.058	0.6514	0.9102	1.042	0.9739	436.8
1	38.90	39.24	0.16	1509.1	1503.1	1.033	1.046	0.5919	0.8921	1.051	0.9785	392.9
					$t = 150$ °C[c]							
1	100.00	100.00	100.00	23.111	23.111	1.000	1.243	0.9914	1.002	1.000	0.8531	208.4
1	95.54	96.15	10.96	207.67	210.80	1.000	1.236	0.9479	0.9902	1.006	0.8570	202.6
1	92.04	93.05	6.36	362.87	363.65	1.000	1.230	0.9157	0.9827	1.010	0.8601	197.4
1	88.71	90.05	4.50	515.38	514.07	1.001	1.224	0.8848	0.9755	1.015	0.8633	192.2
1	84.73	86.38	3.30	698.92	700.07	1.002	1.216	0.8476	0.9665	1.021	0.8671	185.7
1	79.04	80.99	2.36	982.64	977.89	1.004	1.205	0.7942	0.9533	1.030	0.8729	176.0
1	69.57	71.64	1.57	1466.2	1474.3	1.009	1.183	0.7045	0.9298	1.045	0.8834	158.6
1	59.97	61.71	1.14	2025.3	2021.1	1.020	1.158	0.6136	0.9040	1.063	0.8950	139.3

Summary of Infinite Dilution Activity Coefficients of Methylamine in *N*-Methyl-2-pyrrolidone

t/°C	γ^∞
50	1.021
100	1.093
150	1.243

[a] Wilson equation parameters: $\Lambda_{AB} = 0.2069$, $\Lambda_{BA} = 2.1652$. Note: A value of 781.04 kPa was used for the vapor pressure of methylamine in the data reduction procedure. This value was obtained from the correlation reported by Daubert et al. (1991). [b] Wilson equation parameters: $\Lambda_{AB} = 0.3555$, $\Lambda_{BA} = 1.7425$. Note: A value of 2661.1 kPa was used for the vapor pressure of methylamine in the data reduction procedure. This value was obtained from the correlation reported by Daubert et al. (1991). [c] Wilson equation parameters: $\Lambda_{AB} = 0.2989$, $\Lambda_{BA} = 1.6222$. Note: A value of 6644.2 kPa was used for the vapor pressure of methylamine in the data reduction procedure. This value was obtained from the correlation reported by Daubert et al. (1991).

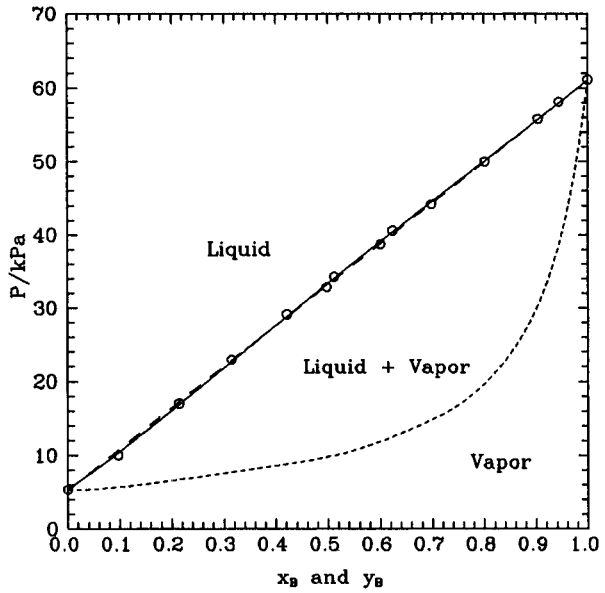

Figure 17. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2,3-dichloro-1-propanol (A) + epichlorohydrin (B) at 100 °C.

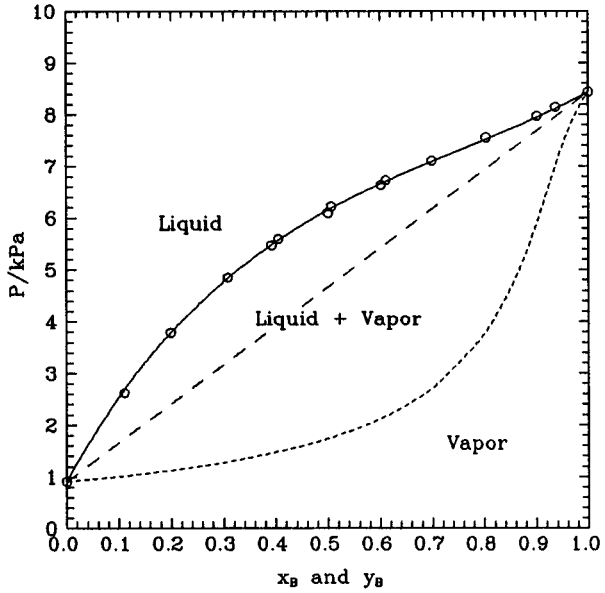

Figure 18. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2,3-epoxy-1-propanol (A) + epichlorohydrin (B) at 50 °C.

Table 13. Liquid−Liquid Equilibrium Data for Triethylene Glycol (A) + 1-Pentene (B)

		mol %		mass %	
	t/°C	A	B	A	B
lower liquid	0.0	94.92 ± 0.04	5.08 ± 0.04	97.56 ± 0.02	2.44 ± 0.02
upper liquid		0.10 ± 0.02	99.90 ± 0.02	0.23 ± 0.04	99.77 ± 0.04
lower liquid	100.0	88.70 ± 0.37	11.30 ± 0.37	94.38 ± 0.20	5.62 ± 0.20
upper liquid		0.81 ± 0.01	99.19 ± 0.01	1.72 ± 0.01	98.28 ± 0.01

Table 14. Constants Used in the Data Reduction Procedure

compound	MW	T_c/K	P_c/kPa	Z_c	ω	ref
ethanethiol	62.136	499.15	5490.0	0.274	0.1921	*a*
propylene	42.081	364.76	4612.6	0.275	0.1424	*a*
nitrobenzene	123.111	719.00	4400.0	0.257	0.4480	*a*
methanol	32.042	512.58	8095.9	0.224	0.5656	*a*
pyridine	79.101	619.95	5633.7	0.278	0.2389	*a*
ethyl acetate	88.106	523.30	3880.0	0.255	0.3664	*a*
n-octane	114.231	568.83	2486.3	0.259	0.3962	*a*
tert-amyl methyl ether	102.177	534.00	3040.0	0.262	0.3011	*a*
diisopropyl ether	102.177	500.05	2877.6	0.267	0.3383	*a*
n-butane	58.123	425.18	3796.9	0.274	0.1993	*a*
epichlorohydrin	92.525	610.00	4900.0	0.225	0.2562	*a*
1,3-dichloro-2-propanol	128.986	634.00	4570.0	0.235	0.7040	*b*
2,3-dichloro-1-propanol	128.986	634.00	4570.0	0.227	0.8020	*b*
2,3-epoxy-1-propanol	74.079	621.10	5900.0	0.231	0.7560	*b*
3-chloro-1,2-propanediol	110.540	653.30	5480.0	0.197	1.1770	*b*
hydrogen cyanide	27.026	456.65	5390.5	0.197	0.4102	*a*
N-methyl-2-pyrrolidone	99.133	724.00	4780.0	0.251	0.3577	*a*
methylamine	31.057	430.05	7457.5	0.321	0.2813	*a*
triethylene glycol	150.175	700.00	3320.0	0.253	1.3863	*a*
1-pentene	70.134	464.78	3528.7	0.270	0.2329	*a*

[a] Measured and/or estimated values reported by Daubert et al. (1991). [b] Estimated using techniques shown in Chapter 2 of Reid et al. (1987).

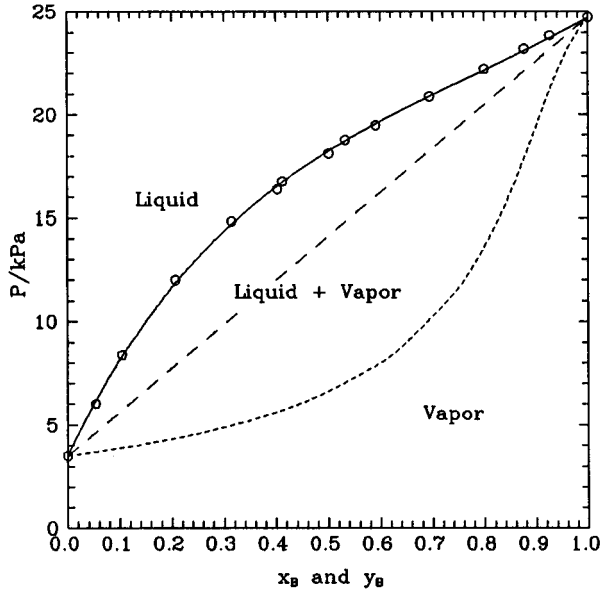

Figure 19. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2,3-epoxy-1-propanol (A) + epichlorohydrin (B) at 75 °C.

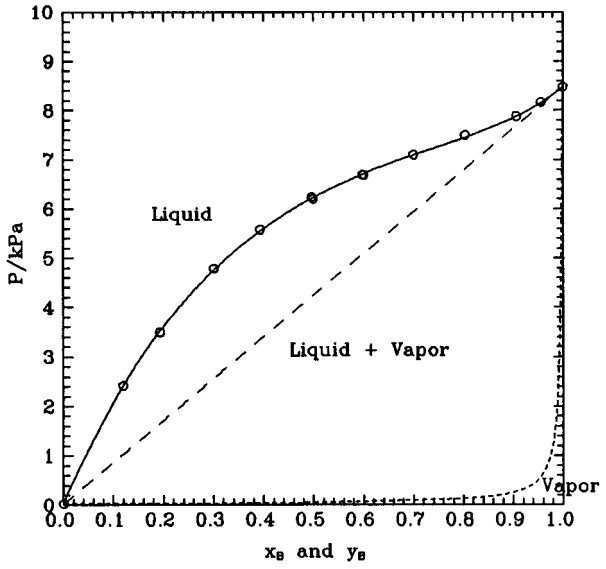

Figure 20. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 3-chloro-1,2-propanediol (A) + epichlorohydrin (B) at 50 °C.

and 1-pentene were not measured in this work, correlations reported by Daubert et al. (1991) give values of 0.0016 and 193.4 kPa, respectively, at 50 °C.

The same procedure was used at 100 °C using a stainless steel apparatus similar to the one shown in Figure 2. The cell was modified to include lines for sampling the upper and lower liquid phases.

PTx Data Reduction Procedure

The results of the *PTx* measurements, which are total pressure as a function of charge composition at constant temperature, were reduced to equilibrium phase compositions, activity coefficients, and fugacity coefficients. Various activity coefficient models were used to represent the liquid-phase nonidealities. The Soave−Redlich−Kwong equation of state (Soave, 1972) was used to represent the vapor phase in the data reduction procedure. All Soave binary interaction parameters were assumed to be zero.

To derive equilibrium phase compositions from *PTx* data, an iterative procedure was used to solve the basic equation of vapor−liquid equilibrium, given as follows:

$$Py_i\phi_i = x_i\gamma_i P_i^{\circ}\phi_i^{\circ} \exp\left[\left(\frac{V_i}{RT}\right)(P - P_i^{\circ})\right] \qquad (1)$$

where P is the total pressure, y_i is the vapor mole fraction

of component i, ϕ_i is the fugacity coefficient of component i, x_i is the liquid mole fraction of component i, γ_i is the activity coefficient of component i, $P_i°$ is the vapor pressure of component i at the system temperature, $\phi_i°$ is the fugacity coefficient of component i at the system temperature and corresponding vapor pressure of component i, and the exponential term is the Poynting correction where V_i is the molar volume of component i. In the above expression it is assumed that the molar volume of component i is equal to the partial molar volume of component i at these conditions. Pure component molar volumes were calculated from correlations of density data (Daubert et al., 1991).

The data reduction procedure, similar to the method proposed by Barker (1953), consisted of fitting the pressure data to eq 1 across the entire composition range by adjusting the parameters of the activity coefficient model. The activity coefficient model that gave the best overall fit of the measured total pressure data for a given system was generally used to reduce the data for that system. The Wilson equation (Wilson, 1964), the three-parameter Redlich−Kister expansion (Prausnitz et al., 1986), and the NRTL equation (Renon and Prausnitz, 1968) were used in the data reduction procedure and are given below:

Wilson equation:

$$\ln \gamma_A = -\ln(x_A + \Lambda_{AB}x_B) + x_B\left(\frac{\Lambda_{AB}}{x_A + \Lambda_{AB}x_B} - \frac{\Lambda_{BA}}{\Lambda_{BA}x_A + x_B}\right) \quad (2)$$

$$\ln \gamma_B = -\ln(x_B + \Lambda_{BA}x_A) - x_A\left(\frac{\Lambda_{AB}}{x_A + \Lambda_{AB}x_B} - \frac{\Lambda_{BA}}{\Lambda_{BA}x_A + x_B}\right)$$

Redlich−Kister equation:

$$\ln \gamma_A = x_B^2[(A + 3B + 5C) - (4B + 16C)x_B + 12Cx_B^2] \quad (3)$$

$$\ln \gamma_B = x_A^2[(A - 3B + 5C) + (4B - 16C)x_A + 12Cx_A^2]$$

NRTL equation:

$$\ln \gamma_A = x_B^2\left[\tau_{BA}\left(\frac{G_{BA}}{x_A + x_BG_{BA}}\right)^2 + \left(\frac{\tau_{AB}G_{AB}}{(x_B + x_AG_{AB})^2}\right)\right] \quad (4)$$

$$\ln \gamma_B = x_A^2\left[\tau_{AB}\left(\frac{G_{AB}}{x_B + x_AG_{AB}}\right)^2 + \left(\frac{\tau_{BA}G_{BA}}{(x_A + x_BG_{BA})^2}\right)\right]$$

$$G_{AB} = \exp(-\alpha\tau_{AB})$$

$$G_{BA} = \exp(-\alpha\tau_{BA})$$

As a beginning point, the ideal-solution parameters of the activity coefficient model were selected. Then assuming the liquid composition was the same as the charge composition and the fugacity coefficients were unity, eq 1 was solved for the product Py_i for each component. The calculated pressure was then the sum of these terms:

$$P_{calc} = \sum(Py_i) \quad (5)$$

Table 15. Comparison of Measured and Literature Vapor Pressures

		P/kPa		
compound	t/°C	meas	lit.[a]	% dev[b]
ethanethiol	−20.0	8.810	9.098	−3.16
	50.3	165.65	166.27	−0.37
propylene	−20.0	306.04	308.12	−0.67
	50.3	2058.8	2056.6	0.11
nitrobenzene	50.3	0.203	0.199	2.01
	150.0	18.856	19.302	−2.31
methanol	0.0	4.009	3.939	1.78
	50.3	56.421	56.195	0.40
	75.0	150.51	150.76	−0.17
	150.0	1413.1	1389.1	1.73
pyridine	50.3	9.773	9.698	0.77
	150.0	251.74	253.20	−0.58
ethyl acetate	50.3	38.484	38.069	1.09
	150.0	695.54	689.46	0.88
octane	50.0	6.684	6.645	0.55
	150.0	189.46	192.20	−1.43
tert-amyl methyl ether	50.0	29.300	28.906	1.36
	150.0	500.41	493.29	1.44
diisopropyl ether	0.0	5.757	5.977	−3.68
	100.0	250.07	255.05	−1.95
butane	0.0	103.14	103.59	−0.44
	100.0	1531.5	1527.8	0.24
epichlorohydrin	50.0	8.409	7.984	5.32
		8.471	7.984	6.09
		8.434	7.984	5.63
		8.479	7.984	6.19
	75.0	24.733	23.450	5.47
	100.0	61.076	58.270	4.81
		61.119	58.270	4.89
		61.124	58.270	4.90
1,3-dichloro-2-propanol	50.0	0.584		
	100.0	7.926		
2,3-dichloro-1-propanol	50.0	0.352		
	100.0	5.353		
2,3-epoxy-1-propanol	50.0	0.910		
	75.0	3.512		
3-chloro-1,2-propanediol	50.0	0.026		
	100.0	0.726		
hydrogen cyanide	0.0	35.221	35.258	−0.10
	75.0	482.36	491.36	−1.83
N-methyl-2-pyrrolidone	50.0	*c*	0.249	
	100.0	*c*	3.434	
	150.0	*c*	23.111	
methylamine	50.0	*c*	781.04	
	100.0	*c*	2661.1	
	150.0	*c*	6644.2	

[a] Literature data calculated from correlations from correlations in Daubert et al. (1991). [b] Percent deviation: 100 × (measured-literature)/literature. [c] The vapor pressures of these compounds were not measured by Wiltec. The literature values shown in the table were used in the data reduction.

The vapor mole fraction for each component was then determined:

$$y_i = (Py_i)/P_{calc} \quad (6)$$

With values for the vapor-phase composition, the fugacity coefficients were calculated from the equation of state.

The next step was to correct the liquid composition for the amounts of each component in the vapor and to return to the step in which the activity coefficients were calculated and continue iterating until the calculated pressure converged. As part of each iteration step, the amount of material taken out of the cell as degas was subtracted from the total charge at the calculated vapor composition.

This procedure was performed for each of the measurement points across the composition range. The calculated pressures were compared to the measured pressures. The activity coefficient parameters were adjusted to improve the fit of the total pressure data, and the entire procedure

was repeated until the best fit of the measured total pressure curve was obtained.

Results and Discussion

The results of the phase equilibrium measurements are described below. The *PTx* data are presented in tables which give the run number, the charge compositions (z_A), the calculated liquid (x_A) and vapor compositions (y_A), the measured and correlated pressures, the activity (γ_A and γ_B) and fugacity coefficients (ϕ_A and ϕ_B) obtained from the correlation, the Poynting corrections (PF_A and PF_B), and the relative volatilities (α_{BA}). The relative volatility was determined from

$$\alpha_{BA} = \frac{y_B/x_B}{y_A/x_A} \tag{7}$$

The activity coefficient parameters used to obtain the correlation are given at the bottom of each table. A table summarizing the values of γ^∞ methylamine in *N*-methyl-2-pyrrolidone at each of the three temperatures is also included. Figures showing total pressure as a function of liquid and vapor composition are included to illustrate the data. Liquid−liquid equilibrium measurement results are shown in tabular form giving the results of the sample analyses and the accuracy of the determinations.

1. Ethanethiol + Propylene. Results of *PTx* measurements on ethanethiol + propylene at −20 and 50 °C are given in Table 1. The Wilson activity coefficient equation was used to reduce the data. These data are plotted in Figures 4 and 5. The activity coefficients are greater than unity at both temperatures. The −20 °C isotherm shows a positive deviation from Raoult's law. Raoult's law is defined here by the expression $P = \sum(P_i^\circ x_i)$, where P is the total system pressure, P_i° is the vapor pressure of component i, and x_i is the liquid mole fraction of component i. At 50 °C there is significant nonideality in the vapor phase, causing the total pressure plot to lie below Raoult's law in the propylene-rich region of the system.

2. Nitrobenzene + Methanol. *PTx* measurements on nitrobenzene + methanol were performed at 50.3 and 150 °C. The NRTL activity coefficient equation was used to reduce the data. Results of the measurements are given in Table 2 and plotted in Figures 6 and 7. This system shows significant positive deviation from ideality.

3. Pyridine + Ethyl Acetate. Results of pyridine + ethyl acetate *PTx* measurements at 50.3 and 150 °C are reported in Table 3. The data were reduced using the Wilson activity coefficient equation. This system exhibits nearly ideal behavior at the measurement conditions. The results are plotted in Figures 8 and 9.

4. Octane + tert-Amyl Methyl Ether. Octane + *tert*-amyl methyl ether also shows nearly ideal behavior at the temperatures studied, 50 and 150 °C. Results of the *PTx* measurements are listed in Table 4 and are plotted in Figures 10 and 11. The Wilson activity coefficient equation was used to reduce the data.

5. Diisopropyl Ether + Butane. *PTx* data for diisopropyl ether + butane were obtained at 0 and 100 °C. These data are reported in Table 5 and Figures 12 and 13. The data were reduced using the Wilson activity coefficient equation. This system also shows nearly ideal behavior with activity coefficients slightly greater than unity. At 0 °C the total pressure is just above Raoult's law on the diisopropyl ether-rich half of the binary and right on Raoult's law on the butane-rich half. The vapor-phase nonidealities cause the total pressure to be below Raoult's law at the higher temperature of 100 °C.

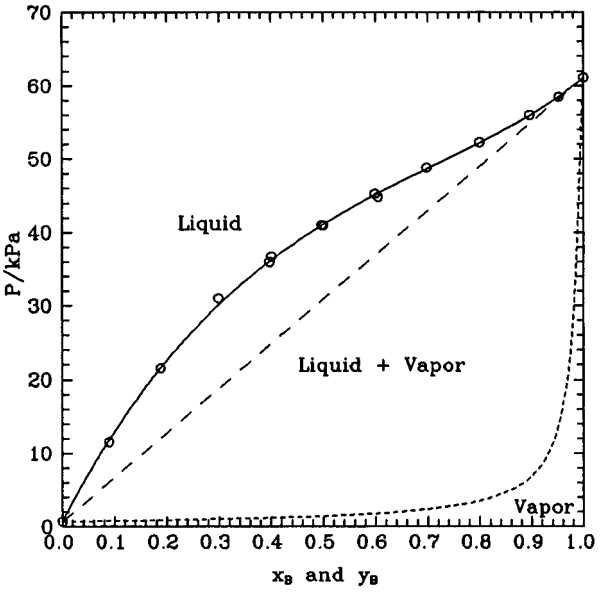

Figure 21. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 3-chloro-1,2-propanediol (A) + epichlorohydrin (B) at 100 °C.

6. 1,3-Dichloro-2-propanol + Epichlorohydrin. Results of *PTx* measurements on 1,3-dichloro-2-propanol + epichlorohydrin at 50 and 100 °C are given in Table 6. The NRTL activity coefficient equation was used to reduce the data. This system exhibits slight negative deviation from Raoult's law. Figures 14 and 15 show plots of these data.

7. 2,3-Dichloro-1-propanol + Epichlorohydrin. Slight deviation from Raoult's law is exhibited by 2,3-dichloro-1-propanol + epichlorohydrin at 50 and 100 °C. The *PTx* measurement results are listed in Table 7 and plotted in Figures 16 and 17. These data were reduced using the Redlich−Kister activity coefficient equation.

8. 2,3-Epoxy-1-propanol + Epichlorohydrin. *PTx* data were obtained for 2,3-epoxy-1-propanol (23E1P) + epichlorohydrin at 50 and 75 °C. These data are reported in Table 8 and are plotted in Figures 18 and 19. The NRTL activity coefficient equation was used to reduce the data. This system exhibits positive deviation from ideality. Measurements were attempted at 100 °C but were not possible due to instability in the 23E1P at this temperature.

The vapor pressure of 23E1P was difficult to measure, even at the lower temperatures of 50 and 75 °C. Several degasses were required before the pressure leveled off at the reported value. Although the vapor pressures reported here were carefully measured, a more in depth study of the vapor pressure of 23E1P may be desirable.

9. 3-Chloro-1,2-propanediol + Epichlorohydrin. The 3-chloro-1,2-propanediol + epichlorohydrin system also shows positive deviation from ideality at 50 and 100 °C. Results of the *PTx* measurements are reported in Table 9 and plotted in Figures 20 and 21. The data were reduced using the NRTL activity coefficient equation. For this system, the vapor pressure of 3-chloro-1,2-propanediol was measured at several different temperatures. These measurements were combined with 3-chloro-1,2-propanediol vapor pressure data obtained by Wiltec in conjunction with DIPPR Project 805(E)/90 (Wilding and Wilson, 1994). These data were then fitted to the Antoine equation. This information along with the resulting fit is shown in Table 10.

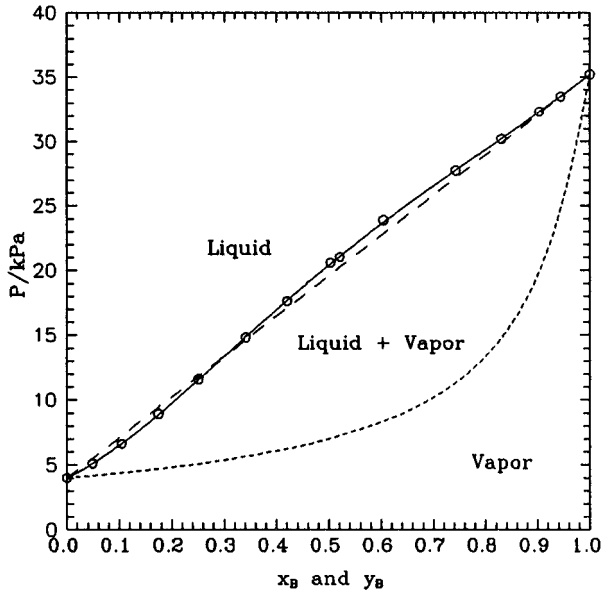

Figure 22. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for methanol (A) + hydrogen cyanide (B) at 0 °C.

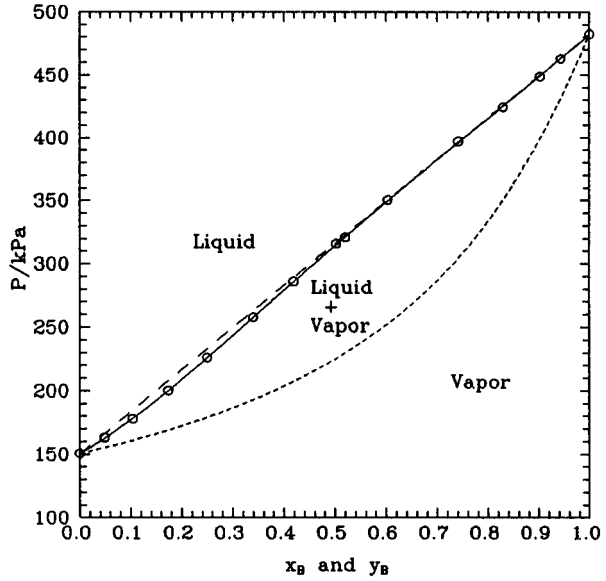

Figure 23. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for methanol (A) + hydrogen cyanide (B) at 75 °C.

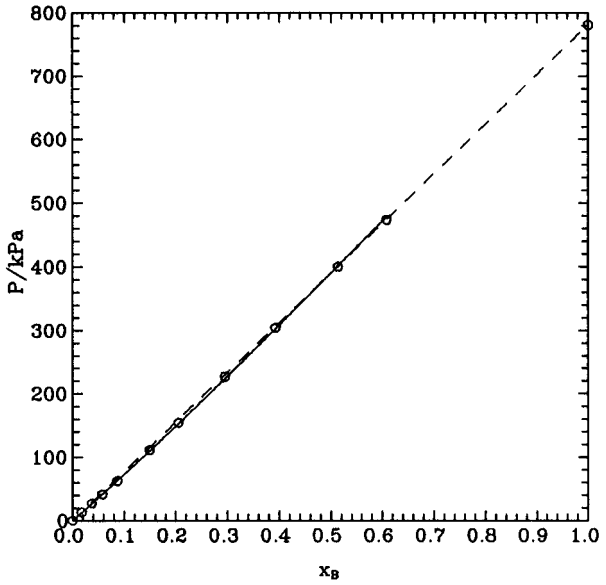

Figure 24. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for *N*-methyl-2-pyrrolidone (A) + methylamine (B) at 50 °C.

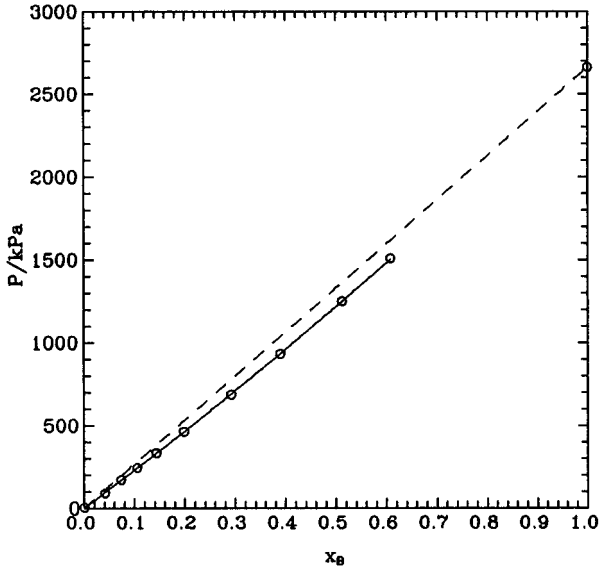

Figure 25. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for *N*-methyl-2-pyrrolidone (A) + methylamine (B) at 100 °C.

10. Methanol + Hydrogen Cyanide. *PTx* measurements on methanol + hydrogen cyanide were performed at 0 and 75 °C. The three-parameter Redlich−Kister activity coefficient equation was used to reduce the data. Results of the measurements are given in Table 11. Plots of these data can be found in Figures 22 and 23. This system shows nearly ideal behavior at both temperatures. Regions of both slightly negative and slightly positive deviation from Raoult's law can be seen in the *P*−*x* plots.

11. N-Methyl-2-pyrrolidone + Methylamine. The infinite dilution activity coefficient (γ^{∞}) of methylamine in *N*-methyl-2-pyrrolidone (NMP) was determined at 50, 100, and 150 °C. These values were determined by making *PTx* measurements on the NMP-rich half of the binary and reducing the data using literature values for the vapor pressure of both components and the Wilson activity coefficient equation. Results of the *PTx* measurements are reported in Table 12. *P*−*x* plots of these data are shown in Figures 24 through 26. A summary of γ^{∞} for methylamine at each of the temperatures is shown at the bottom of Table 12.

Determination of γ^{∞} using gas chromatographic retention times was originally attempted with this system. However, reliable results were not obtained due to a strong dependency of the retention time with the sample injection size. This problem is presumably due to the high polarity of the NMP and methylamine. The retention-time technique did exhibit the same trend seen in the results reported here; i.e., the value of γ^{∞} for methylamine moved away from unity as the temperature increased from 50 to 150 °C.

12. Triethylene Glycol + 1-Pentene. The triethylene glycol + 1-pentene system exhibits immiscible regions at 0 and 100 °C. Liquid−liquid equilibrium measurements were performed and are reported in Table 13.

Ancillary Data. Table 14 gives the physical constants for each compound used in the data reduction procedure. Table 15 compares the measured pure component vapor pressures to correlations reported by Daubert et al. (1991).

Table 16. Source and Purity of Chemicals Used for Measurements

compound	CAS No.[a]	supplier	purity, mass %	
			Wiltec analysis	supplier analysis
ethanethiol	75-08-1	Kodak		99.9+
propylene	115-07-1	Matheson	99.9+	99.0+[b]
nitrobenzene	98-95-3	Aldrich	99.9+	99.9
methanol	65-56-1	Aldrich	99.9+	99.99+
pyridine	110-86-1	Aldrich	99.9+	99.9+
ethyl acetate	141-78-6	Aldrich	99.9	99.9
n-octane	111-65-9	Aldrich	99.5	99.4
tert-amyl methyl ether	994-05-8	Aldrich	99.4[c]	98.8
diisopropyl ether	108-20-3	Aldrich	99.9	99.0
n-butane	106-97-8	Phillips	99.9	99.9
epichlorohydrin	106-89-8	Aldrich		99.9
1,3-dichloro-2-propanol	96-23-1	Aldrich		99.5
2,3-dichloro-1-propanol	616-23-1	Kodak		99.6
2,3-epoxy-1-propanol	556-52-5	Aldrich		98.2
3-chloro-1,2-propanediol	96-24-2	Aldrich		99.1
hydrogen cyanide	74-90-8	FUMICO		99.6[d]
N-methyl-2-pyrrolidone	872-50-4	Aldrich		99.3
methylamine	74-89-5	Aldrich	99.9+	99.9[d]
triethylene glycol	112-27-6	Aldrich	99.9+	99.7
1-pentene	109-67-1	Aldrich	99.9	99.6

[a] Supplied by the authors. [b] This is a specification rather than an actual lot analysis. [c] This value was obtained after Wiltec distilled the chemical sent by the supplier. The Wiltec analysis before distillation was 98.6%. [d] These are typical analyses rather than actual lot analyses.

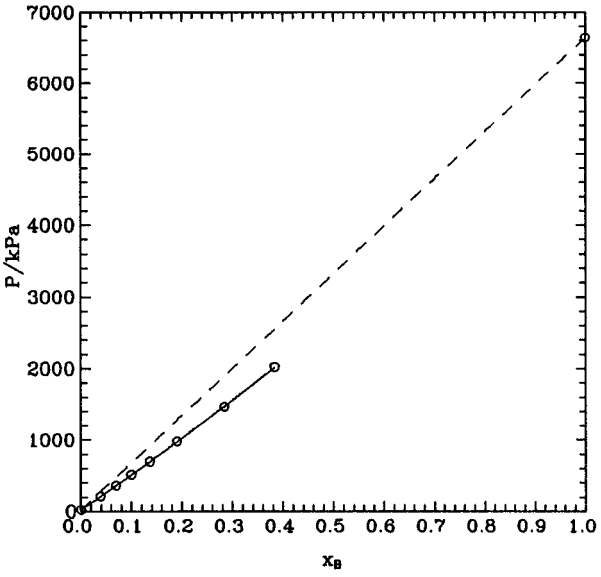

Figure 26. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for *N*-methyl-2-pyrrolidone (A) + methylamine (B) at 150 °C.

Table 16 lists the Chemical Abstracts number, source, and purity of the chemicals used in this study. The chemicals were degassed before being used whenever possible. The *tert*-amyl methyl ether received from the supplier was purified by distillation before being used.

Acknowledgment

We wish to thank Mark B. Swenson for his assistance in measuring these data.

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