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Phase Equilibria on Four Binary Systems: 1,2-Dichloroethane + *trans*-1,2-Dichloroethylene, 1-Octene + 2-Methyl Thiophene, 2-Ethyl Thiophene + 2,2,4-Trimethylpentane, and Cyclopropanecarbonitrile + Water[†]

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Phase equilibria are reported for the following four systems: 1,2-dichloroethane (CASRN 107-06-2) + *trans*-1,2-dichloroethylene (CASRN 156-60-5) at 30 °C and 80 °C; 1-octene (CASRN 111-66-0) + 2-methyl thiophene (CASRN 554-14-3) at 100 °C and 140 °C; 2-ethyl thiophene (CASRN 872-55-9) + 2,2,4-trimethylpentane (CASRN 540-84-1) at 100 °C and 140 °C; cyclopropanecarbonitrile (CASRN 5500-21-0) + water (CASRN 7732-18-5) at 100 °C and 135 °C. The system pressure and temperature were measured at several charge compositions along a given isotherm for each system. Equilibrium vapor- and liquid-phase compositions were derived from the measured *PTx* data using the Soave equation of state to represent the vapor phase and the NRTL activity coefficient model to represent the liquid phase. Two liquid phases are present with the cyclopropanecarbonitrile + water system at 100 °C. Vapor−liquid−liquid equilibrium data were measured at this condition. Multiple samples were withdrawn and analyzed from each equilibrium phase. A second liquid phase is not present with this system at 135 °C. *PTxy* measurements were performed at this temperature in order to better define the azeotropic composition. Multiple samples were withdrawn and analyzed from the equilibrium vapor and liquid phases at three liquid compositions near the azeotrope.

Introduction

This work is part of an ongoing investigation of phase equilibria for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Properties, DIPPR, of the American Institute of Chemical Engineers. This paper reports measurements that have been made under Project 805/01 to obtain phase equilibrium data on four binary systems. These systems and their measurement temperatures are as follows:

1. 1,2-Dichloroethane + *trans*-1,2-dichloroethylene at 30 °C and 80 °C.
2. 1-Octene + 2-methyl thiophene at 100 °C and 140 °C.
3. 2-Ethyl thiophene + 2,2,4-trimethylpentane at 100 °C and 140 °C.
4. Cyclopropanecarbonitrile + water at 100 °C and 135 °C.

Vapor−liquid equilibria (VLE) were determined for all four 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 nonidealities in the vapor phase, and an activity coefficient equation was used to represent the nonidealities in the liquid phase.

Two liquid phases are present in the cyclopropanecarbonitrile + water (system 4) at 100 °C. Vapor−liquid−liquid equilibrium (VLLE) data were obtained at this condition by directly measuring the composition of both liquid phases and the vapor phase. *PTxy* data were obtained for this same system at 135 °C by directly measuring the composition of the equilibrium vapor and liquid phases at three charge compositions.

Experimental Section

The apparatus and procedures used for the *PTx* measurements have been described previously.[1] Temperatures were measured with platinum resistance thermometers that were calibrated using ice and steam points and referenced to a standard resistance thermometer with a NIST traceable calibration. Temperatures were measured with a precision of ± 0.01 K and an uncertainty of ± 0.05 K or better using ITS-90.

PTx measurements were performed using a glass cell apparatus on the lower isotherm of systems 1 through 3, as well as run 3 of the lower isotherm of system 4. Pressures measured using this apparatus have an estimated uncertainty of ± 0.04 kPa.

PTx measurements on the upper isotherm of systems 1 through 3 as well as runs 1 and 2 of both the upper and lower isotherms of system 4 were performed using a stainless steel apparatus. Pressures were measured using a calibrated Paroscientific pressure transducer with an estimated uncertainty of ± 0.5 kPa.

PTx measurements on run 3 of the upper isotherm of system 4 were performed using the apparatus shown in Figure 1. This apparatus consisted of a 395 cm^3 cell made from thick-walled glass pipe and sealed on the top and bottom with flanges. Liquid and vapor sampling lines and a pressure measurement line extended through the top of the cell. The liquid in the cell was vigorously stirred with a magnetically coupled stir bar. The pressure was measured using a calibrated pressure transducer manufactured by Paroscientific. Pressures were measured in this apparatus with an estimated uncertainty of ± 0.5 kPa.

This apparatus was used to visually observe the contents of the equilibrium cell at pressures higher than those that can be

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[†] This contribution will be part of a special print edition containing papers reporting experimental results from the various projects of the Design Institute for Physical Properties of the American Institute of Chemical Engineers.

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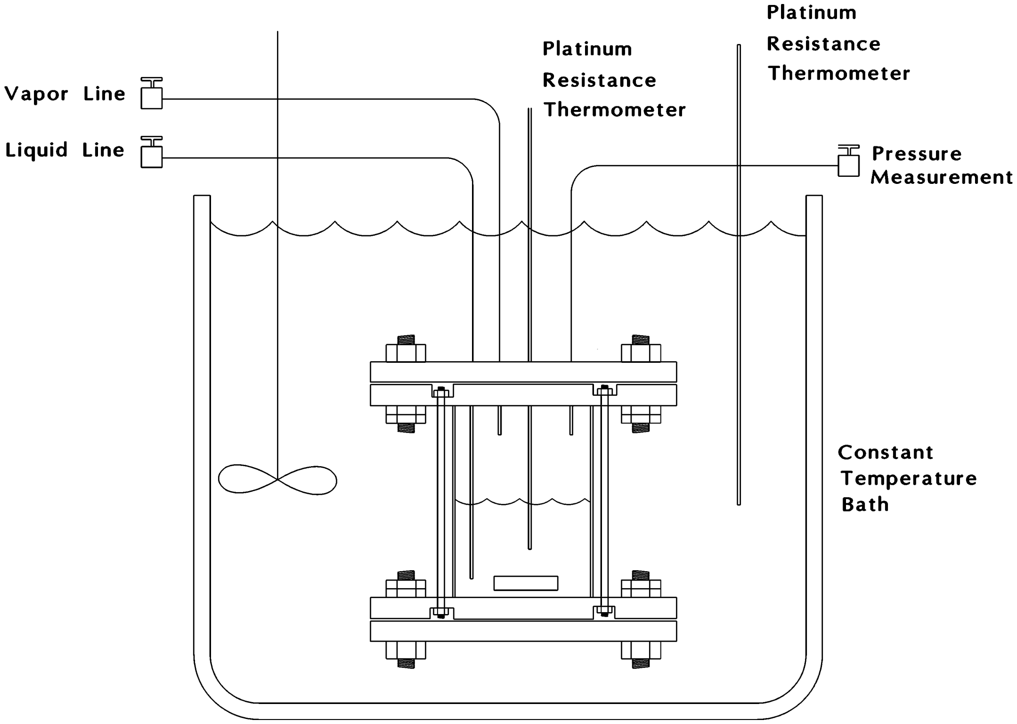

Figure 1. Glass pipe apparatus used for *PTx* and *PTxy* measurements.

Table 1. *PTx* Measurement Results on 1,2-Dichloroethane (A) + *trans*-1,2-Dichloroethylene (B)

run	$100z_A$	$100x_A$	$100y_A$	P/kPa measd	P/kPa calcd	γ_A	γ_B	φ_A	φ_B	PF_A	PF_B	α_{BA}
						t = 30 °C[a]						
1	100.00	100.00	100.00	13.28	13.28	1.000	1.336	0.995	0.996	1.0000	0.9988	5.295
1	97.56	97.58	88.51	14.65	14.65	1.000	1.319	0.994	0.996	1.0000	0.9988	5.227
1	95.21	95.24	79.48	15.98	15.94	1.001	1.303	0.994	0.995	1.0001	0.9988	5.161
1	92.85	92.89	71.94	17.19	17.20	1.001	1.288	0.993	0.995	1.0001	0.9989	5.095
1	90.35	90.40	65.19	18.56	18.50	1.002	1.272	0.993	0.995	1.0002	0.9989	5.026
1	85.40	85.47	54.59	20.97	20.98	1.006	1.242	0.992	0.994	1.0002	0.9990	4.891
1	80.57	80.64	46.66	23.24	23.29	1.010	1.215	0.991	0.993	1.0003	0.9991	4.761
1	71.01	71.08	35.28	27.49	27.55	1.024	1.166	0.989	0.992	1.0005	0.9992	4.509
1	60.75	60.82	26.76	31.73	31.77	1.045	1.121	0.988	0.991	1.0006	0.9993	4.248
2	58.07	58.11	24.92	32.90	32.83	1.051	1.111	0.987	0.990	1.0006	0.9994	4.180
2	52.73	52.78	21.64	34.92	34.86	1.066	1.091	0.986	0.990	1.0007	0.9994	4.049
1	48.96	49.01	19.54	36.21	36.26	1.078	1.079	0.986	0.989	1.0007	0.9995	3.957
1	44.43	44.47	17.22	37.81	37.91	1.094	1.065	0.985	0.989	1.0008	0.9995	3.849
2	42.31	42.37	16.21	38.73	38.66	1.102	1.059	0.985	0.989	1.0008	0.9995	3.799
2	31.45	31.52	11.48	42.52	42.46	1.150	1.033	0.984	0.988	1.0009	0.9997	3.549
2	20.89	20.95	7.40	46.06	46.09	1.210	1.015	0.982	0.986	1.0010	0.9998	3.315
2	15.68	15.72	5.51	47.93	47.87	1.244	1.008	0.982	0.986	1.0011	0.9998	3.202
2	10.48	10.51	3.66	49.82	49.66	1.282	1.004	0.981	0.985	1.0012	0.9999	3.092
2	5.25	5.27	1.83	51.57	51.48	1.325	1.001	0.980	0.985	1.0012	0.9999	2.984
2	2.61	2.63	0.91	52.51	52.40	1.348	1.000	0.980	0.985	1.0012	1.0000	2.931
2	0.00	0.00	0.00	53.33	53.33	1.372	1.000	0.979	0.984	1.0013	1.0000	2.878
						t = 80 °C[b]						
1	100.00	100.00	100.00	90.9	90.9	1.000	1.227	0.976	0.983	1.0000	0.9949	3.494
1	97.77	97.81	92.80	95.4	96.0	1.000	1.219	0.975	0.982	1.0001	0.9950	3.470
1	95.42	95.50	86.05	101.1	101.3	1.000	1.211	0.974	0.981	1.0003	0.9952	3.444
1	90.89	91.05	74.99	111.3	111.2	1.001	1.195	0.971	0.979	1.0006	0.9954	3.393
1	86.18	86.40	65.54	121.1	121.3	1.003	1.178	0.969	0.977	1.0009	0.9957	3.339
1	81.45	81.70	57.63	131.3	131.2	1.006	1.163	0.966	0.975	1.0012	0.9960	3.283
1	71.11	71.39	44.14	152.5	151.9	1.015	1.129	0.961	0.971	1.0018	0.9966	3.157
1	60.68	60.92	34.03	171.5	171.6	1.029	1.098	0.956	0.967	1.0023	0.9972	3.023
2	59.95	60.11	33.35	173.3	173.1	1.031	1.096	0.956	0.967	1.0024	0.9972	3.012
2	54.42	54.62	29.05	183.0	182.9	1.041	1.081	0.953	0.965	1.0027	0.9975	2.939
1	50.58	50.76	26.31	189.3	189.6	1.050	1.071	0.951	0.963	1.0029	0.9977	2.887
1	45.52	45.67	22.98	198.0	198.2	1.063	1.059	0.949	0.962	1.0031	0.9979	2.818
2	43.65	43.91	21.89	201.1	201.2	1.068	1.055	0.949	0.961	1.0032	0.9980	2.793
2	32.58	32.85	15.65	218.9	219.2	1.106	1.032	0.944	0.958	1.0037	0.9985	2.637
2	21.46	21.69	10.07	236.1	236.6	1.157	1.015	0.940	0.954	1.0042	0.9990	2.475
2	15.63	15.82	7.30	245.7	245.7	1.191	1.008	0.938	0.953	1.0045	0.9993	2.387
2	10.08	10.21	4.71	254.3	254.2	1.228	1.003	0.935	0.951	1.0047	0.9996	2.303
2	5.47	5.54	2.56	262.0	261.4	1.264	1.001	0.934	0.950	1.0050	0.9998	2.232
2	2.64	2.68	1.24	266.6	265.7	1.287	1.000	0.933	0.949	1.0051	0.9999	2.189
2	0.00	0.00	0.00	269.9	269.9	1.311	1.000	0.932	0.948	1.0052	1.0000	2.148

[a] NRTL parameters: $\tau_{AB} = 0.0120$, $\tau_{BA} = 0.3044$, $\alpha = 0.3$. [b] NRTL parameters: $\tau_{AB} = -0.2779$, $\tau_{BA} = 0.5732$, $\alpha = 0.3$.

measured using the glass cell apparatus. Run 3 measurements were performed at liquid compositions ranging from a mole fraction of about 0.11 water to a mole fraction of about 0.96 water. Visual observations that were made during the course

Table 2. *PTx* Measurement Results on 1-Octene (A) + 2-Methyl Thiophene (B)

				P/kPa								
run	$100z_A$	$100x_A$	$100y_A$	measd	calcd	γ_A	γ_B	φ_A	φ_B	PF_A	PF_B	α_{BA}
						t = 100 °C[a]						
1	100.00	100.00	100.00	53.82	53.82	1.000	1.260	0.974	0.985	1.0000	0.9995	1.624
1	97.38	97.39	95.86	54.77	54.72	1.000	1.252	0.974	0.985	1.0000	0.9995	1.614
1	94.78	94.80	91.92	55.63	55.58	1.000	1.244	0.973	0.985	1.0001	0.9995	1.603
1	89.89	89.92	84.94	57.15	57.16	1.001	1.229	0.972	0.984	1.0002	0.9996	1.582
1	84.99	85.04	78.47	58.60	58.66	1.003	1.214	0.972	0.984	1.0003	0.9996	1.559
1	80.12	80.17	72.49	59.99	60.08	1.006	1.198	0.971	0.983	1.0003	0.9997	1.534
1	69.50	69.55	60.77	62.87	62.88	1.016	1.163	0.970	0.982	1.0005	0.9998	1.474
1	59.10	59.14	50.71	65.20	65.24	1.033	1.129	0.969	0.981	1.0006	0.9998	1.407
1	48.94	48.97	41.86	67.14	67.14	1.059	1.096	0.968	0.980	1.0007	0.9999	1.333
2	39.49	39.51	34.21	68.82	68.56	1.095	1.068	0.968	0.980	1.0008	1.0000	1.256
2	29.51	29.53	26.41	69.78	69.66	1.149	1.041	0.967	0.980	1.0009	1.0000	1.168
2	19.47	19.48	18.42	70.24	70.33	1.226	1.020	0.967	0.979	1.0009	1.0000	1.071
2	14.58	14.58	14.31	70.32	70.47	1.275	1.012	0.967	0.979	1.0009	1.0000	1.022
2	9.87	9.87	10.11	70.30	70.46	1.331	1.006	0.968	0.979	1.0009	1.0000	0.973
2	5.15	5.14	5.55	70.18	70.29	1.398	1.002	0.968	0.979	1.0009	1.0000	0.923
2	2.68	2.68	2.98	70.13	70.12	1.438	1.000	0.968	0.979	1.0009	1.0000	0.897
2	0.00	0.00	0.00	69.87	69.87	1.485	1.000	0.968	0.979	1.0009	1.0000	0.868
						t = 140 °C[b]						
1	100.00	100.00	100.00	165.9	165.9	1.000	1.175	0.941	0.966	1.0000	0.9986	1.463
1	97.32	97.34	96.17	167.9	168.1	1.000	1.170	0.940	0.966	1.0001	0.9986	1.457
1	94.71	94.75	92.56	170.1	170.2	1.000	1.165	0.939	0.965	1.0002	0.9987	1.451
1	90.05	90.11	86.36	173.7	173.8	1.001	1.157	0.938	0.964	1.0004	0.9988	1.439
1	84.32	84.39	79.17	178.5	178.1	1.002	1.146	0.937	0.962	1.0007	0.9990	1.423
1	79.00	79.09	72.90	182.2	182.0	1.004	1.135	0.935	0.961	1.0009	0.9991	1.406
1	69.04	69.12	62.03	188.4	188.6	1.011	1.113	0.933	0.959	1.0012	0.9993	1.370
1	58.98	59.05	52.07	194.4	194.6	1.023	1.091	0.932	0.958	1.0015	0.9995	1.327
1	48.38	48.42	42.41	199.9	200.0	1.042	1.068	0.930	0.956	1.0018	0.9997	1.275
1	43.16	43.19	37.89	202.2	202.3	1.055	1.057	0.930	0.955	1.0020	0.9998	1.246
2	31.59	31.64	28.25	206.5	206.5	1.094	1.034	0.929	0.954	1.0022	0.9999	1.175
2	20.73	20.76	19.23	209.1	209.1	1.150	1.016	0.928	0.953	1.0023	1.0000	1.100
2	15.85	15.86	15.06	209.9	209.9	1.182	1.010	0.928	0.953	1.0024	1.0000	1.064
2	10.13	10.14	9.97	210.6	210.4	1.228	1.004	0.928	0.953	1.0024	1.0000	1.019
2	5.05	5.05	5.16	210.4	210.3	1.277	1.001	0.929	0.953	1.0024	1.0000	0.977
2	2.53	2.52	2.64	210.3	210.1	1.305	1.000	0.929	0.953	1.0024	1.0000	0.955
2	0.00	0.00	0.00	209.8	209.8	1.335	1.000	0.929	0.953	1.0024	1.0000	0.934

[a] NRTL parameters: $\tau_{AB} = -0.4922$, $\tau_{BA} = 0.9661$, $\alpha = 0.3$. [b] NRTL parameters: $\tau_{AB} = -0.5370$, $\tau_{BA} = 0.9197$, $\alpha = 0.3$.

of this run confirmed that a single liquid phase was present at this temperature over the composition range that was studied.

VLLE measurements on system 4 at 100 °C were performed using a glass cell apparatus similar to the one used for the *PTx* measurements. The cell had an internal volume of about 300 cm^3 and was equipped with vapor, lower-liquid, and upper-liquid sampling lines. The system pressure was measured with an attached mercury manometer that extended from the side of the cell with an estimated uncertainty of ± 0.04 kPa.

The VLLE measurements were initiated by charging the cell with appropriate amounts of water and cyclopropanecarbonitrile. The cell and its contents were then brought to equilibrium at 100 °C. The liquid in the cell was vigorously stirred with a magnetic stir bar. After the system had equilibrated at 100 °C, the cell contents were degassed by removing vapor into a weighed receiver, and the system pressure was measured. Additional vapor was removed as degas until a stable system pressure was obtained.

Five vapor samples were withdrawn into weighed, evacuated sample vials. The system was allowed to re-equilibrate to the run temperature between each of the vapor samples. The stirrer was then turned off, and the two liquid phases were allowed to settle. Each of the liquid sample lines was then purged. Three samples were then removed from the lower-liquid phase into weighed, evacuated sample vials; four samples were removed from the upper-liquid phase into weighed syringes. The stirrer was turned back on, and three additional vapor samples were withdrawn into weighed syringes.

The five vapor samples that were taken into sample vials and the lower-liquid samples were analyzed for cyclopropanecarbonitrile by gas chromatography (GC) using a flame ionization detector. A known mass of ethanol was carefully weighed into each sample as an internal standard. Three or more injections of each sample were made onto the GC column, and the average results were used to determine the composition of each sample. The average of the analysis results of the replicate samples from the vapor and lower-liquid phases was used to determine the equilibrium phase compositions. The analysis results of the replicate samples agreed to within ± 1.5 % of the reported value.

Multiple calibration standards covering the composition range of the samples were carefully prepared gravimetrically maintaining approximately the same ratio of ethanol to sample that was present in the actual samples. These standards were analyzed by GC in conjunction with the actual samples. The GC response factor that was determined for each calibration standard agreed to within ± 1 % of the average of all of the standards.

The upper-liquid samples and the three vapor samples that were taken into syringes were analyzed for water by Karl Fischer titration. The entire sample was injected into the titration beaker and titrated to dryness. The titrant was carefully standardized before performing these measurements. The analysis results of the replicate vapor samples agreed to within ± 1 % of their average value while the results of the replicate upper-liquid samples agreed to within ± 0.2 %. The concentration of cyclopropanecarbonitrile in the vapor determined by difference from Karl Fischer water analysis (mole fraction of 0.2216) agreed reasonably well with the results obtained directly by GC analysis (mole fraction of 0.2180). The average of these values (mole fraction of 0.2198) is reported in Table 4.

The measured vapor and lower-liquid cyclopropanecarbonitrile compositions have an estimated uncertainty of ± 2 % of their reported values. The measured upper-liquid water composition has an estimated uncertainty of ± 1 % of the reported

Table 3. *PTx* Measurement Results on 2-Ethyl Thiophene (A) + 2,2,4-Trimethylpentane (B)

				P/kPa								
run	$100z_A$	$100x_A$	$100y_A$	measd	calcd	γ_A	γ_B	φ_A	φ_B	PF_A	PF_B	α_{BA}
						t = 100 °C[a]						
1	100.00	100.00	100.00	33.26	33.26	1.000	1.774	0.988	0.986	1.0000	0.9959	5.330
1	97.54	97.60	88.76	36.64	36.64	1.000	1.715	0.986	0.984	1.0001	0.9961	5.151
1	95.20	95.31	80.30	39.52	39.65	1.002	1.663	0.985	0.983	1.0003	0.9962	4.990
1	90.49	90.68	67.50	45.21	45.18	1.006	1.567	0.983	0.981	1.0005	0.9966	4.685
1	86.03	86.27	58.70	49.90	49.85	1.013	1.488	0.982	0.979	1.0007	0.9968	4.421
1	81.85	82.11	52.26	53.86	53.83	1.021	1.423	0.980	0.977	1.0008	0.9971	4.193
1	71.73	71.99	40.93	62.17	62.20	1.051	1.294	0.977	0.973	1.0011	0.9976	3.710
1	61.64	61.86	32.89	69.28	69.28	1.091	1.199	0.975	0.970	1.0014	0.9980	3.310
1	51.32	51.48	26.32	75.74	75.72	1.144	1.127	0.972	0.968	1.0017	0.9984	2.970
2	41.70	41.82	21.00	81.04	81.25	1.203	1.078	0.970	0.965	1.0019	0.9987	2.704
1	41.41	41.51	20.84	81.43	81.43	1.205	1.077	0.970	0.965	1.0019	0.9987	2.696
2	36.45	36.57	18.29	84.03	84.14	1.239	1.058	0.969	0.964	1.0020	0.9989	2.576
1	35.37	35.43	17.71	84.78	84.76	1.247	1.054	0.969	0.964	1.0020	0.9989	2.549
2	31.24	31.36	15.67	87.01	86.96	1.278	1.041	0.968	0.963	1.0021	0.9990	2.459
2	20.73	20.83	10.47	92.60	92.56	1.365	1.017	0.966	0.961	1.0024	0.9994	2.250
2	14.77	14.85	7.51	95.92	95.71	1.419	1.008	0.965	0.959	1.0025	0.9995	2.146
2	9.29	9.35	4.77	98.72	98.59	1.473	1.003	0.964	0.958	1.0026	0.9997	2.057
2	5.13	5.16	2.65	100.94	100.78	1.516	1.001	0.963	0.957	1.0027	0.9998	1.995
2	2.62	2.63	1.36	102.24	102.11	1.543	1.000	0.963	0.956	1.0027	0.9999	1.959
2	0.00	0.00	0.00	103.49	103.49	1.572	1.000	0.962	0.956	1.0028	1.0000	1.922
						t = 140 °C[b]						
1	100.00	100.00	100.00	111.4	111.4	1.000	1.624	0.969	0.965	1.0000	0.9903	3.855
1	97.48	97.62	91.65	119.2	118.9	1.000	1.577	0.967	0.963	1.0003	0.9907	3.744
1	95.08	95.35	84.92	125.7	125.8	1.001	1.535	0.965	0.960	1.0005	0.9911	3.642
1	90.76	91.20	74.92	137.5	137.3	1.005	1.465	0.962	0.957	1.0010	0.9917	3.468
1	86.23	86.79	66.58	148.5	148.4	1.010	1.401	0.959	0.953	1.0014	0.9924	3.299
1	81.84	82.47	59.93	158.6	158.4	1.018	1.345	0.956	0.950	1.0018	0.9929	3.147
1	71.32	71.99	47.63	178.8	179.5	1.043	1.236	0.950	0.943	1.0026	0.9941	2.825
1	60.52	61.09	38.10	197.7	198.4	1.080	1.154	0.945	0.937	1.0033	0.9952	2.551
1	50.20	50.62	30.53	214.4	214.6	1.124	1.097	0.941	0.932	1.0039	0.9961	2.332
2	42.68	42.93	25.53	226.1	225.7	1.161	1.066	0.938	0.929	1.0043	0.9967	2.195
1	39.72	39.97	23.68	229.7	229.9	1.177	1.056	0.937	0.927	1.0045	0.9970	2.146
2	37.03	37.29	22.04	233.9	233.6	1.191	1.048	0.936	0.926	1.0046	0.9972	2.104
1	34.35	34.52	20.36	237.5	237.5	1.207	1.040	0.934	0.925	1.0047	0.9974	2.062
2	31.39	31.65	18.64	241.9	241.4	1.224	1.033	0.933	0.924	1.0049	0.9976	2.021
2	20.27	20.49	12.07	256.8	256.3	1.294	1.013	0.929	0.919	1.0054	0.9985	1.877
2	15.24	15.41	9.11	263.1	262.9	1.328	1.007	0.928	0.917	1.0057	0.9989	1.819
2	10.50	10.63	6.30	269.3	269.2	1.362	1.003	0.926	0.915	1.0059	0.9992	1.768
2	5.37	5.45	3.25	275.8	275.8	1.400	1.001	0.924	0.913	1.0062	0.9996	1.717
2	2.73	2.77	1.65	279.0	279.3	1.420	1.000	0.923	0.912	1.0063	0.9998	1.691
2	0.00	0.00	0.00	282.8	282.8	1.441	1.000	0.922	0.911	1.0064	1.0000	1.667

[a] NRTL parameters: $\tau_{AB} = 0.6751$, $\tau_{BA} = -0.0988$, $\alpha = 0.3$. [b] NRTL parameters: $\tau_{AB} = 0.6986$, $\tau_{BA} = -0.2011$, $\alpha = 0.3$.

value. These estimates are based on the agreement between multiple samples taken from the same phase at the same condition and on results obtained by analyzing standards of known composition using the same analytical techniques.

PTxy measurements on system 4 at 135 °C were performed using the thick-walled glass pipe apparatus shown in Figure 1. The cell was charged with appropriate amounts of water and cyclopropanecarbonitrile and the system was brought to equilibrium at 135 °C. Three vapor and three liquid samples were taken at each condition using the procedures described above for the VLLE measurements. Both the vapor and liquid samples were analyzed by GC for cyclopropanecarbonitrile. The measured composition of cyclopropanecarbonitrile in the vapor and in the liquid has an estimated uncertainty of ± 1.5 % of the reported value. These estimates are based on the agreement between multiple samples taken from the same phase at the same condition and on results obtained by analyzing standards of known composition using the same analytical techniques.

PTx Data Reduction Procedure

The results of the *PTx* measurements, which are total pressure as a function of charge composition at constant temperature and known cell volume, were reduced to equilibrium phase compositions and activity and fugacity coefficients. The Soave−Redlich−Kwong equation of state[2] was used to represent the vapor phase while the NRTL[3] or Wilson[4] activity coefficient equations were used to represent the liquid-phase non-idealities in the data reduction procedure. The measured data for all four systems were reduced using the NRTL equation. The measured results at 135 °C on system 4 were also reduced using the Wilson activity coefficient equation. The Soave binary interaction parameters used in the data reduction procedure were assumed to be zero. The procedure used to reduce the *PTx* data has been previously described[1] and is similar to the method proposed by Barker.[5]

Results and Discussion

The results of the phase equilibrium measurements are described below. The *PTx* data for systems 1 through 4 are presented in Tables 1 through 4 and Table 6. The results obtained by reducing the measured *PTx* and *PTxy* data on system 4 at 100 °C and 135 °C with the NRTL equation are shown in Table 4. Table 6 contains the results obtained by reducing the measured *PTx* and *PTxy* data on system 4 with the Wilson activity coefficient equation at 135 °C. The tables give the run numbers, the charge compositions (z_A), the calculated liquid (x_A) and vapor (y_A) compositions, the measured and correlated pressures, the activity (γ_A and γ_B) and fugacity coefficients (φ_A and φ_B), the Poynting corrections (PF_A and PF_B), and the relative volatilities (α_{BA}) of the lighter compound (B) over the heavier compound (A). The compositions are reported on a mole basis. The activity coefficient parameters used in the correlation are given in the footnotes of each table.

The results of the measured VLLE data for system 4 at 100 °C are shown as run 4 in Table 4. *PTxy* data for system 4 at 135 °C are shown in Tables 5 and 7. The tables reporting the

Table 4. *PTx* and VLLE Measurement Results on Cyclopropanecarbonitrile (A) + Water (B) NRTL Activity Coefficient Equation Used in the Data Reduction

				P/kPa								
run	$100z_A$	$100x_A$	$100y_A$	measd	calcd	γ_A	γ_B	φ_A	φ_B	PF_A	PF_B	α_{BA}
						$t = 100$ °C[a]						
1	100.00	100.00	100.00	35.2	35.2	1.000	7.482	0.987	1.001	1.0000	0.9996	21.311
1	96.76	96.89	62.57	50.9	55.1	1.002	6.585	0.981	0.998	1.0005	0.9997	18.651
3	95.10	95.33	53.86	58.1	63.2	1.004	6.197	0.978	0.997	1.0007	0.9998	17.481
1	93.68	93.89	48.24	66.1	69.9	1.008	5.872	0.977	0.996	1.0009	0.9998	16.493
1	90.91	91.18	41.08	77.6	80.6	1.015	5.328	0.974	0.995	1.0012	0.9999	14.820
1	88.55	88.84	37.00	86.5	88.2	1.024	4.923	0.972	0.994	1.0014	0.9999	13.555
3	87.37	87.75	35.50	90.4	91.3	1.029	4.752	0.971	0.994	1.0015	0.9999	13.014
1	86.13	86.44	33.95	94.3	94.7	1.036	4.558	0.970	0.993	1.0016	1.0000	12.400
1	84.06	84.38	31.94	99.9	99.4	1.047	4.279	0.969	0.993	1.0017	1.0000	11.506
1	81.93	82.24	30.28	104.6	103.7	1.060	4.020	0.968	0.992	1.0018	1.0000	10.667
1	79.20	79.51	28.58	109.3	108.3	1.079	3.725	0.967	0.992	1.0019	1.0000	9.700
3	77.26	77.65	27.62	111.0	110.9	1.094	3.545	0.966	0.992	1.0020	1.0001	9.103
1	75.03	75.33	26.62	115.1	113.8	1.114	3.340	0.965	0.991	1.0021	1.0001	8.418
3	73.37	73.74	26.02	116.1	115.6	1.129	3.212	0.965	0.991	1.0021	1.0001	7.984
1	70.90	71.18	25.18	119.1	118.1	1.156	3.022	0.964	0.991	1.0022	1.0001	7.336
3	68.54	68.88	24.54	120.5	120.0	1.182	2.867	0.964	0.991	1.0022	1.0001	6.804
1	66.79	67.03	24.09	122.0	121.3	1.205	2.753	0.963	0.991	1.0023	1.0001	6.408
3	63.15	63.44	23.33	123.9	123.5	1.255	2.551	0.963	0.991	1.0023	1.0001	5.701
1	62.48	62.69	23.20	124.0	123.9	1.266	2.513	0.963	0.990	1.0023	1.0001	5.564
1	58.62	58.81	22.56	124.9	125.6	1.330	2.326	0.963	0.990	1.0024	1.0001	4.901
3	56.79	57.02	22.31	126.2	126.3	1.364	2.248	0.962	0.990	1.0024	1.0001	4.620
4[b]		**55.34**	**22.10**	**126.9**	**126.8**							**4.368**
3	51.88	52.06	22.10	126.9	126.8	1.471	2.053	0.962	0.990	1.0024	1.0001	3.828
4[b]		**4.25**	**22.10**	**126.9**	**126.8**							**0.156**
2	3.61	3.55	20.89	125.1	125.2	20.330	1.012	0.963	0.990	1.0024	1.0001	0.140
2	1.76	1.72	14.80	118.5	117.5	28.042	1.003	0.967	0.991	1.0022	1.0001	0.101
2	0.89	0.87	9.28	112.6	110.9	33.087	1.001	0.970	0.991	1.0020	1.0001	0.085
2	0.00	0.00	0.00	101.4	101.4	39.601	1.000	0.974	0.992	1.0017	1.0000	0.072
						$t = 135$ °C[c]						
1	100.00	100.00	100.00	102.2	102.2	1.000	7.185	0.971	1.003	1.0000	0.9988	21.440
1	96.76	97.09	64.64	141.3	156.2	1.002	6.177	0.957	0.996	1.0014	0.9991	18.241
1	93.68	94.21	50.83	176.4	195.9	1.008	5.397	0.949	0.992	1.0024	0.9994	15.745
1	90.92	91.57	43.89	205.3	224.0	1.017	4.820	0.943	0.989	1.0031	0.9995	13.883
1	88.57	89.27	39.91	228.1	243.6	1.027	4.404	0.939	0.988	1.0036	0.9996	12.527
3	87.54	89.12	39.70	231.7	244.7	1.028	4.379	0.939	0.988	1.0036	0.9996	12.444
1	86.16	86.90	36.94	249.9	260.2	1.039	4.039	0.936	0.986	1.0040	0.9997	11.328
1	84.10	84.86	34.96	266.6	272.4	1.051	3.767	0.933	0.985	1.0043	0.9998	10.426
1	81.98	82.73	33.29	282.0	283.2	1.065	3.520	0.931	0.985	1.0046	0.9998	9.600
1	79.25	79.99	31.56	297.9	295.1	1.085	3.245	0.929	0.984	1.0049	0.9999	8.671
1	75.09	75.80	29.49	318.1	310.0	1.120	2.898	0.926	0.982	1.0052	1.0000	7.486
3	73.76	75.36	29.31	320.2	311.3	1.124	2.866	0.926	0.982	1.0053	1.0000	7.376
1	70.97	71.61	27.89	333.5	321.8	1.161	2.621	0.924	0.982	1.0055	1.0001	6.522
1	66.86	67.44	26.57	346.3	331.6	1.208	2.396	0.922	0.981	1.0058	1.0001	5.723
1	62.55	63.06	25.39	355.8	340.2	1.264	2.199	0.921	0.980	1.0060	1.0002	5.015
3	58.42	59.49	24.54	357.8	346.2	1.316	2.063	0.920	0.980	1.0062	1.0002	4.515
1	58.71	59.17	24.47	362.4	346.7	1.321	2.052	0.920	0.980	1.0062	1.0002	4.473
3	53.57	54.47	23.47	364.9	353.3	1.401	1.899	0.919	0.979	1.0063	1.0002	3.901
1	53.80	54.17	23.41	368.0	353.7	1.406	1.890	0.919	0.979	1.0064	1.0002	3.867
3	48.92	49.65	22.55	370.2	359.0	1.499	1.764	0.918	0.978	1.0065	1.0003	3.386
1	43.24	43.45	21.52	374.1	364.6	1.658	1.616	0.917	0.978	1.0066	1.0003	2.803
3	42.55	43.07	21.46	373.8	364.9	1.669	1.608	0.917	0.978	1.0066	1.0003	2.769
3	37.60	37.97	20.73	375.1	368.1	1.845	1.502	0.917	0.978	1.0067	1.0003	2.340
1	32.17	32.25	20.07	375.8	370.5	2.115	1.395	0.917	0.977	1.0068	1.0003	1.896
3	31.53	31.75	20.02	375.8	370.6	2.144	1.386	0.917	0.977	1.0068	1.0003	1.859
1	26.47	26.50	19.58	376.2	371.6	2.519	1.298	0.917	0.977	1.0068	1.0003	1.481
3	25.57	25.66	19.53	376.2	371.7	2.595	1.284	0.917	0.977	1.0068	1.0003	1.423
1	21.06	21.06	19.32	376.4	371.9	3.130	1.213	0.917	0.977	1.0068	1.0003	1.115
3	19.94	19.95	19.29	376.2	371.9	3.300	1.197	0.917	0.977	1.0068	1.0003	1.043
2	15.33	15.30	19.22	376.5	371.9	4.286	1.132	0.917	0.977	1.0068	1.0003	0.760
3	14.52	14.48	19.21	376.2	371.9	4.526	1.121	0.917	0.977	1.0068	1.0003	0.712
1	14.09	14.08	19.20	376.5	371.9	4.654	1.116	0.917	0.977	1.0068	1.0003	0.690
2	13.21	13.16	19.18	376.1	371.9	4.972	1.105	0.917	0.977	1.0068	1.0003	0.639
2	11.00	10.93	19.07	376.0	371.7	5.948	1.078	0.917	0.977	1.0068	1.0003	0.521
3	9.28	9.24	18.86	376.0	371.2	6.953	1.059	0.917	0.977	1.0068	1.0003	0.438
3	8.95	8.91	18.80	376.1	371.1	7.187	1.056	0.917	0.977	1.0068	1.0003	0.423
2	8.75	8.67	18.75	375.6	370.9	7.362	1.053	0.917	0.977	1.0068	1.0003	0.412
2	7.02	6.93	18.18	374.6	369.4	8.912	1.036	0.918	0.977	1.0068	1.0003	0.335
2	5.31	5.20	17.08	372.5	366.1	11.060	1.022	0.919	0.977	1.0067	1.0003	0.266
3	4.21	4.19	15.98	369.7	362.6	12.735	1.015	0.920	0.977	1.0066	1.0003	0.230
2	3.61	3.51	14.94	366.5	359.2	14.117	1.011	0.922	0.978	1.0065	1.0003	0.207
2	1.76	1.68	10.12	350.9	343.3	19.162	1.003	0.928	0.978	1.0061	1.0002	0.152
2	0.89	0.85	6.14	336.7	330.7	22.444	1.001	0.932	0.979	1.0058	1.0001	0.130
2	0.00	0.00	0.00	312.4	312.4	26.657	1.000	0.939	0.980	1.0053	1.0000	0.110

[a] NRTL parameters: $\tau_{AB} = 1.1591$, $\tau_{BA} = 2.9665$, $\alpha = 0.42$. [b] The results of the VLLE measurement are reported as run 4. The measured liquid composition and system pressure are shown at each liquid boundary together with the pressure and vapor composition obtained from the correlation. The measured vapor composition obtained from the VLLE measurement was a mole fraction of **0.2198 cyclopropanecarbonitrile**. The NRTL parameters were obtained by correlating the measured VLLE data. [c] NRTL parameters: $\tau_{AB} = 1.3013$, $\tau_{BA} = 2.6216$, $\alpha = 0.52$.

Table 5. *PTxy* Measurement Results on Cyclopropanecarbonitrile (A) + Water (B) at 135 °C[a]

P/kPa		$100x_A$	$100y_A$		α_{BA}	
measured	correlated	measured	measured	correlated	measured	correlated
376.1	371.1	8.954	18.825	18.804	0.424	0.425
375.6	372.0	17.511	19.100	19.242	0.899	0.891
376.6	371.8	24.130	19.559	19.440	1.308	1.318

[a] The measured *PTx* and *PTxy* data at 135 °C were correlated using the NRTL equation. The correlated values shown above were obtained at the measured liquid compositions using the NRTL parameters at 135 °C shown in Table 4.

PTxy data list the measured temperature, the measured liquid and vapor composition on a mole basis, the vapor composition determined from the correlations, and the relative volatility of water over cyclopropanecarbonitrile obtained from the measured data and from the correlations. The correlated values were obtained at the measured liquid compositions using the NRTL (Table 4) or Wilson equation (Table 6) parameters shown for the 135 °C measurements.

Figures showing total pressure as a function of liquid and vapor composition are included to illustrate the data. A plot of the vapor composition as a function of liquid composition is also included for the cyclopropanecarbonitrile + water system at 135 °C.

1,2-Dichloroethane + trans-1,2-Dichloroethylene. The results of the *PTx* measurements on 1,2-dichloroethane + *trans*-1,2-dichloroethylene at 30 °C and 80 °C are given in Table 1, and the NRTL parameters are given in the table footnote. The system pressure as a function of liquid and vapor composition at 80 °C is plotted in Figure 2 to illustrate the data. This system exhibits slight positive deviation from ideality with infinite dilution activity coefficients in the range of about 1.2 to 1.4 for both compounds at these temperatures.

1-Octene + 2-Methyl Thiophene. *PTx* measurements on 1-octene + 2-methyl thiophene were performed at 100 °C and 140 °C. The results of these measurements are shown in Table 2 with the NRTL parameters listed in the table footnote. Figure 3 plots the system pressure as a function of the liquid and vapor compositions at 140 °C.

This system also exhibits slight positive deviation from ideality with infinite dilution activity coefficients in the range of about 1.2 to 1.5 for both compounds at these temperatures. However, the ratio of the vapor pressure of these two compounds is only about 1.30 at 100 °C and 1.26 at 140 °C. Therefore, an azeotrope exists for this binary system at these temperatures. The reduced *PTx* data indicate that the azeotrope occurs at a mole fraction of approximately 0.875 2-methyl thiophene at 100 °C and at a mole fraction of about 0.922 2-methyl thiophene at 140 °C.

2-Ethyl Thiophene + 2,2,4-Trimethylpentane. The results of the *PTx* measurements on 2-ethyl thiophene + 2,2,4-

Table 6. *PTx* Measurement Results on Cyclopropanecarbonitrile (A) + Water (B) Wilson Activity Coefficient Equation used in the Data Reduction

				P/kPa								
run	$100z_A$	$100x_A$	$100y_A$	measd	calcd	γ_A	γ_B	φ_A	φ_B	PF_A	PF_B	α_{BA}
						$t = 135$ °C[a]						
1	100.00	100.00	100.00	102.2	102.2	1.000	6.097	0.971	1.003	1.0000	0.9988	18.194
1	96.76	97.05	66.94	141.3	150.5	1.002	5.502	0.959	0.996	1.0012	0.9991	16.273
1	93.68	94.17	52.45	176.4	189.0	1.006	5.005	0.950	0.993	1.0022	0.9993	14.653
1	90.92	91.54	44.75	205.3	218.2	1.012	4.610	0.944	0.990	1.0029	0.9995	13.356
1	88.57	89.26	40.21	228.1	239.7	1.020	4.308	0.940	0.988	1.0035	0.9996	12.351
3	87.53	89.08	39.92	231.7	241.2	1.020	4.287	0.939	0.988	1.0035	0.9996	12.280
1	86.16	86.90	36.76	249.9	258.8	1.029	4.029	0.936	0.986	1.0040	0.9997	11.414
1	84.10	84.87	34.44	266.6	273.2	1.038	3.811	0.933	0.985	1.0043	0.9998	10.675
1	81.98	82.75	32.50	282.0	286.3	1.050	3.604	0.931	0.984	1.0046	0.9999	9.968
1	79.25	80.02	30.48	297.9	300.8	1.066	3.362	0.928	0.983	1.0050	0.9999	9.136
1	75.09	75.84	28.15	318.1	318.9	1.097	3.041	0.925	0.982	1.0055	1.0000	8.011
3	73.84	75.54	28.01	320.2	320.0	1.100	3.020	0.924	0.982	1.0055	1.0000	7.937
1	70.97	71.66	26.42	333.5	332.9	1.134	2.769	0.922	0.981	1.0058	1.0001	7.041
1	66.86	67.49	25.10	346.3	343.9	1.179	2.535	0.920	0.980	1.0061	1.0002	6.194
1	62.55	63.10	24.00	355.8	352.8	1.235	2.324	0.919	0.979	1.0063	1.0002	5.414
3	58.53	59.69	23.31	357.8	358.3	1.286	2.179	0.918	0.979	1.0065	1.0003	4.873
1	58.71	59.20	23.21	362.4	359.0	1.294	2.160	0.918	0.979	1.0065	1.0003	4.800
3	53.71	54.68	22.46	364.9	364.6	1.375	1.993	0.917	0.978	1.0066	1.0003	4.165
1	53.80	54.20	22.39	368.1	365.1	1.384	1.976	0.917	0.978	1.0066	1.0003	4.102
3	49.06	49.84	21.80	370.2	369.1	1.480	1.838	0.916	0.978	1.0067	1.0003	3.565
1	43.24	43.46	21.09	374.1	373.3	1.660	1.663	0.915	0.977	1.0068	1.0003	2.876
3	42.68	43.23	21.07	373.8	373.4	1.668	1.657	0.915	0.977	1.0069	1.0003	2.853
3	37.71	38.09	20.61	375.1	375.6	1.861	1.537	0.915	0.977	1.0069	1.0003	2.371
1	32.17	32.25	20.16	375.8	377.1	2.160	1.418	0.915	0.977	1.0069	1.0004	1.885
3	31.62	31.84	20.14	375.8	377.2	2.185	1.410	0.915	0.977	1.0069	1.0004	1.853
1	26.47	26.50	19.79	376.2	378.0	2.585	1.316	0.915	0.977	1.0070	1.0004	1.462
3	25.64	25.72	19.74	376.2	378.1	2.657	1.303	0.915	0.977	1.0070	1.0004	1.408
1	21.06	21.06	19.47	376.4	378.4	3.203	1.231	0.915	0.977	1.0070	1.0004	1.104
3	19.98	19.99	19.41	376.2	378.4	3.365	1.216	0.915	0.977	1.0070	1.0004	1.038
2	15.34	15.31	19.13	376.5	378.3	4.330	1.152	0.915	0.977	1.0070	1.0004	0.764
3	14.55	14.51	19.08	376.2	378.2	4.555	1.142	0.915	0.977	1.0070	1.0004	0.720
1	14.09	14.08	19.05	376.5	378.2	4.688	1.137	0.915	0.977	1.0070	1.0004	0.696
2	13.21	13.17	18.99	376.1	378.1	4.996	1.125	0.915	0.977	1.0070	1.0004	0.647
2	11.00	10.94	18.81	376.0	377.8	5.956	1.099	0.916	0.977	1.0070	1.0004	0.530
3	9.30	9.26	18.65	376.0	377.4	6.966	1.079	0.916	0.977	1.0070	1.0004	0.445
3	8.98	8.93	18.61	376.1	377.3	7.205	1.076	0.916	0.977	1.0070	1.0004	0.429
2	8.75	8.67	18.58	375.6	377.2	7.409	1.073	0.916	0.977	1.0069	1.0004	0.416
2	7.02	6.92	18.31	374.6	376.5	9.132	1.054	0.916	0.977	1.0069	1.0004	0.332
2	5.31	5.19	17.87	372.5	375.1	11.847	1.037	0.917	0.977	1.0069	1.0003	0.252
3	4.20	4.18	17.44	369.7	373.7	14.307	1.027	0.917	0.977	1.0069	1.0003	0.207
2	3.61	3.48	17.00	366.5	372.1	16.679	1.021	0.918	0.977	1.0068	1.0003	0.176
2	1.76	1.64	14.26	350.9	361.8	29.024	1.007	0.921	0.977	1.0066	1.0003	0.100
2	0.89	0.80	10.54	336.7	347.8	42.457	1.002	0.926	0.978	1.0062	1.0002	0.069
2	0.00	0.00	0.00	312.4	312.4	71.522	1.000	0.939	0.980	1.0053	1.0000	0.041

[a] Wilson equation parameters: $\Lambda_{AB} = 0.0246$, $\Lambda_{BA} = 0.4350$.

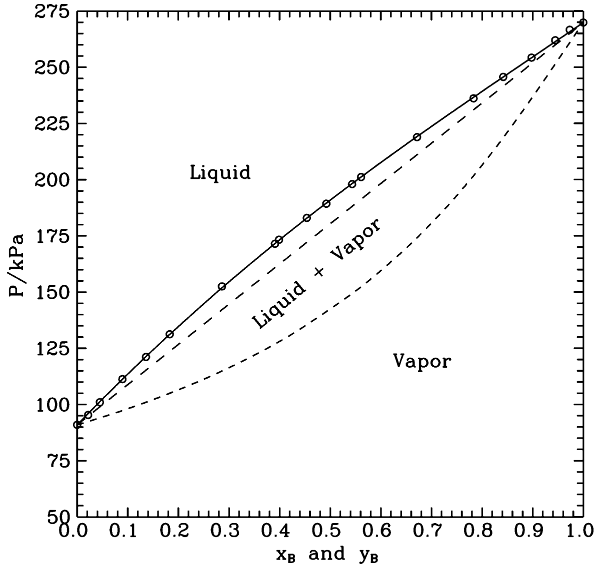

Figure 2. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and − −, Raoult's law for 1,2-dichloroethane (A) + t-1,2-dichloroethylene (B) at 80 °C.

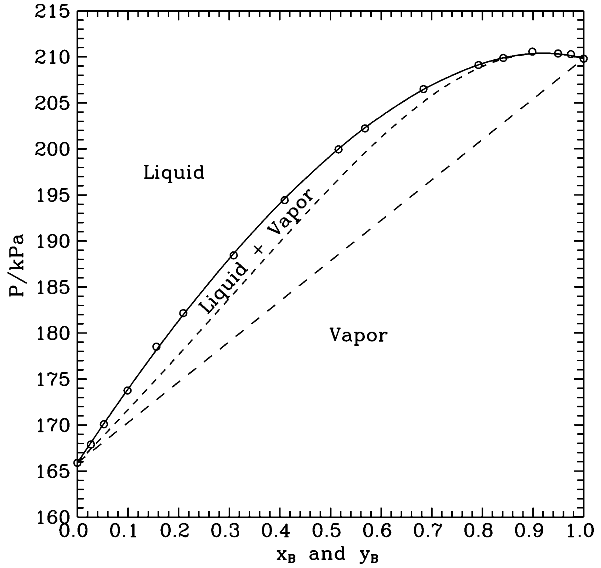

Figure 3. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and − −, Raoult's law for 1-octene (A) + 2-methyl thiophene (B) at 140 °C.

Table 7. *PTxy* Measurement Results on Cyclopropanecarbonitrile (A) + Water (B) at 135 °C using the Wilson Equation[a]

P/kPa		$100x_A$	$100y_A$		α_{BA}	
measured	correlated	measured	measured	correlated	measured	correlated
376.1	377.3	8.954	18.825	18.613	0.424	0.430
375.6	378.3	17.511	19.100	19.262	0.899	0.890
376.6	378.2	24.130	19.559	19.645	1.308	1.301

[a] The measured *PTx* and *PTxy* data at 135 °C were correlated using the Wilson equation. The correlated values shown above were obtained at the measured liquid compositions using the Wilson equation parameters shown in Table 6.

trimethylpentane at 100 °C and 140 °C are reported in Table 3. The NRTL activity coefficient equation parameters are shown in the table footnote. A plot of the system pressure as a function of the liquid and vapor compositions at 140 °C is shown in Figure 4. This system exhibits positive deviation from ideality with infinite dilution activity coefficients of 1.6 and 1.8 at 100 °C and 1.4 and 1.6 at 140 °C for 2-ethyl thiophene and 2,2,4-trimethylpentane, respectively.

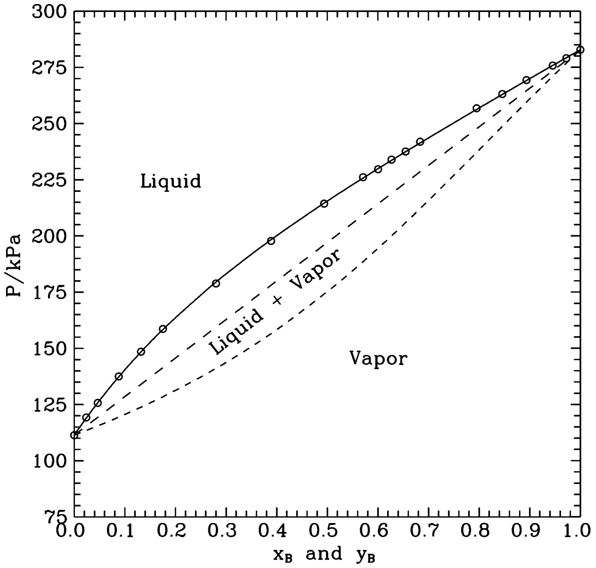

Figure 4. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and − −, Raoult's law for 2-ethyl thiophene (A) + 2,2,4-trimethylpentane (B) at 140 °C.

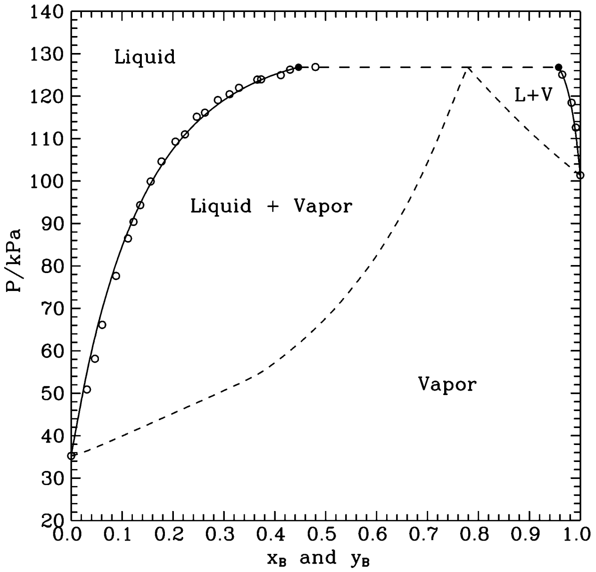

Figure 5. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and ● − − ●, measured VLLE data for cyclopropanecarbonitrile (A) + water (B) at 100 °C.

Cyclopropanecarbonitrile + Water. *PTx* measurements on cyclopropanecarbonitrile + water were performed at 100 °C and 135 °C. VLLE measurements were also performed on this system at 100 °C, and three *PTxy* data points were measured at 135 °C. The measured data at both temperatures were reduced using the NRTL activity coefficient equation, and the results are reported in Tables 4 and 5. The system pressure as a function of liquid and vapor composition at each temperature is plotted in Figures 5 and 6 for the NRTL correlation.

This system exhibits significant positive deviation from ideality. Two liquid phases are present at 100 °C. To better define the liquid−liquid boundaries and the azeotrope at this temperature, VLLE measurements were performed. The measured data were reduced so that the NRTL correlation exactly matched the measured liquid−liquid boundaries. The value of alpha in the NRTL equation was adjusted to fit the measured pressure data and the measured vapor phase composition. The measured compositions of the liquid−liquid boundaries are shown as run 4 in the Table 4 results at 100 °C. Run 4 also

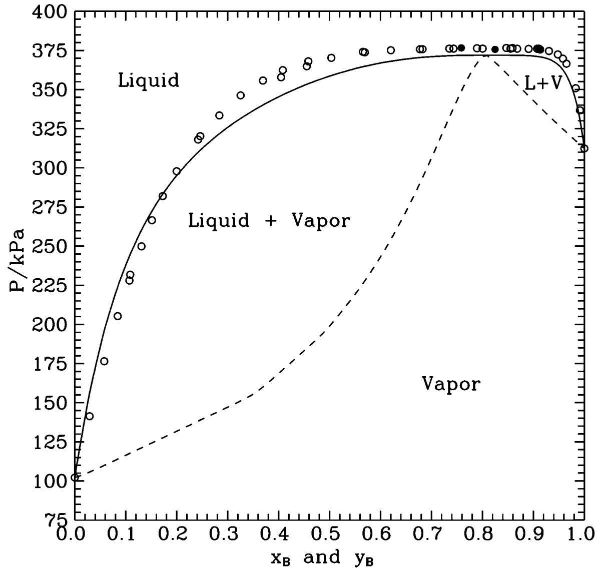

Figure 6. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and ●, measured *PTxy* data for cyclopropanecarbonitrile (A) + water (B) at 135 °C. Data correlated using the NRTL equation.

shows the system pressure and the vapor composition in the immiscible region obtained from the NRTL correlation. The measured vapor composition is shown as a footnote in Table 4.

The results of the measured *PTx* data alone were not adequate to determine whether a second liquid phase was present at 135 °C. A *PTx* run using a visual cell was performed over a composition range from a mole fraction of about 0.11 to 0.96 water. Visual observations indicated that a second liquid phase was not present over the composition range that was studied.

To more accurately define the azeotropic composition of this system at 135 °C, three *PTxy* measurements were performed. The results of the *PTx* data show that the measured pressure varied between 375.8 kPa and 376.5 kPa, less than 0.2 %, over the composition range from a mole fraction of 0.68 to 0.91 water. This relatively wide, flat region of system pressure versus liquid composition made it difficult to accurately determine the azeotropic composition using *PTx* data alone. The *PTxy* measurement results with a comparison to the NRTL correlation are reported at 135 °C in Table 5.

A value of α of 0.52 in the NRTL equation was required to correctly predict a single liquid phase and adequately fit the equilibrium liquid and vapor compositions obtained from the measured *PTxy* data. The resulting NRTL correlation reported in Tables 4 and 5 and shown in Figure 6 does not accurately predict the system pressure that was measured during the *PTx* and *PTxy* runs.

An alternate fit of the measured data at 135 °C was obtained using the Wilson activity coefficient equation. The results and a comparison to this correlation are reported in Tables 6 and 7 and plotted in Figure 7.

The Wilson equation does a better job of fitting the measured *PTx* data while maintaining a good fit of the measured *PTxy* data. The azeotropic composition obtained from the two correlations are nearly the same, a mole fraction of 0.807 water using the NRTL correlation and a mole fraction of 0. 806 water using the Wilson equation correlation. However, the VLE behavior determined from these correlations outside the region of the *PTxy* data varies significantly. Plots of the y−x correlations obtained using the NRTL equation and the Wilson equation are shown in Figure 8. This figure also shows the results of the PTxy measurements.

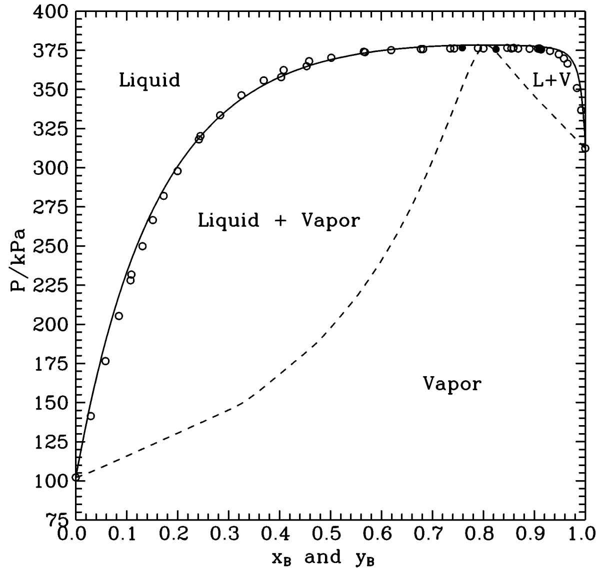

Figure 7. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and ●, measured *PTxy* data for cyclopropanecarbonitrile (A) + water (B) at 135 °C. Data correlated using the Wilson equation.

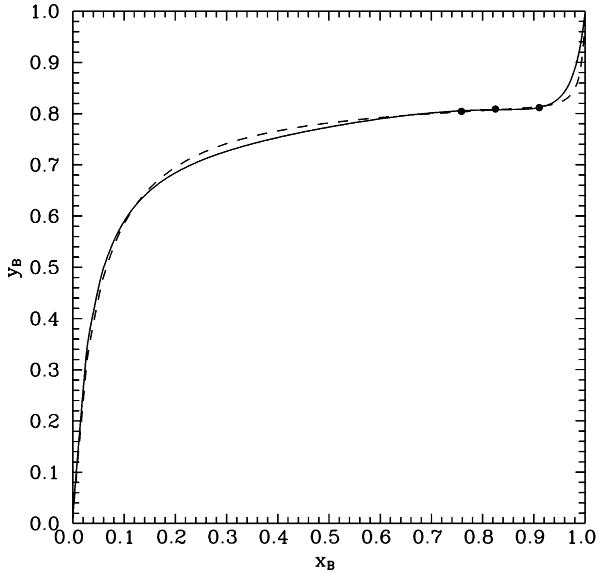

Figure 8. ●, measured *PTxy* data; —, *y*−*x* correlation using the Wilson equation; and - - -, the NRTL equation for cyclopropanecarbonitrile (A) + water (B) at 135 °C.

Table 8. Constants Used in Data Reduction Procedure[a]

compound	MW	T_C/K	P_C/kPa	Z_C	ω
1,2-dichloroethane	98.959	561.6	5370	0.253	0.2866
trans-1,2-dichloroethylene	96.943	516.5	5510	0.287	0.2234
1-octene	112.215	566.9	2663	0.262	0.3921
2-methyl thiophene	98.169	609.0	4910	0.267	0.2389
2-ethyl thiophene	112.194	626.6	4409	0.278	0.2931
2,2,4-trimethylpentane	114.231	543.8	2570	0.266	0.3035
cyclopropanecarbonitrile	67.089	621.9	4462	0.210	0.3415
water	18.015	647.10	22064	0.229	0.3449

[a] Constants are measured and/or estimated values reported in ref 6.

Ancillary Data. Table 8 gives the physical constants for each compound used in the *PTx* data reduction procedure. Table 9 compares the measured pure component vapor pressures to correlations reported in the DIPPR 801 database.[6] Table 10 lists the source and purity of the chemicals used in this study. All of the chemicals were degassed before being used. Table 10

Table 9. Measured and Literature Vapor Pressures

		P/kPa		
compound	*t*/°C	measd	literature[a]	% dev[b]
1,2-dichloroethane	30	13.28	13.42 ± 1 %	−1.0
	80	90.9	90.3 ± 1 %	+0.7
trans-1,2-dichloroethylene	30	53.33	54.03 ± 5 %	−1.3
	80	269.9	265.1 ± 5 %	+1.8
1-octene	100	53.82	53.70 ± 3 %	+0.2
	140	165.9	165.1 ± 3 %	+0.5
2-methyl thiophene	100	69.87	69.78 ± 3 %	+0.1
	140	209.8	208.3 ± 3 %	+0.7
2-ethyl thiophene	100	33.26	35.90 ± 10 %	−7.4
	140	111.4	119.3 ± 10 %	−6.6
2,2,4-trimethylpentane	100	103.49	103.92 ± 3 %	−0.4
	140	282.8	283.2 ± 3 %	−0.1
cyclopropanecarbonitrile	100	35.21	34.83 ± 10 %	+1.1
	135	102.2	101.2 ± 10 %	+1.0
water	100	101.35	101.26 ± 0.2 %	+0.1
	135	312.4	312.6 ± 0.2 %	−0.1

[a] Literature data calculated from correlations in ref 6. [b] Percent deviation: 100 × (measured-literature)/literature.

Table 10. Source and Purity of Chemicals

			mass fraction purity	
compound	CASRN	supplier	Wiltec analysis	supplier analysis
1,2-dichloroethane	107-06-2	Aldrich	0.9999	0.9999
trans-1,2-dichloroethylene	156-60-5	PPG Industries	0.9985	0.998+
1-octene	111-66-0	Aldrich	0.993	0.992
2-methyl thiophene	554-14-3	Aldrich	0.996	0.996
2-ethyl thiophene	872-55-9	Acros Organics	0.985	0.985
2,2,4-trimethylpentane	540-84-1	Aldrich	0.999	0.9983
cyclopropanecarbonitrile	5500-21-0	805 Committee	0.998[a]	0.99+[b]
water	7732-18-5	Shadow Mountain	0.999+	0.999+

[a] A Karl Fischer analysis performed by Wiltec indicated that 0.37 mass % water was present in the chemical sent by the supplier. This water was effectively removed by Wiltec with molecular sieves prior to performing the reported measurements. [b] The supplier did not have an actual lot analysis on the chemical that was sent to Wiltec. Based on information on previous lots of this chemical, the supplier indicated that the purity should be greater than 99 mass % and that the water content should be less than 0.5 mass %.

also lists the Chemical Abstracts Service Registry Number (CASRN) for each chemical.

The 2-ethyl thiophene obtained from the supplier had a mass fraction purity of 0.985. A GC analysis performed by Wiltec indicated that several light and heavy impurities were present in the chemical. Light impurities accounted for about 0.2 % of the total area while the combined area of the heavy impurities was about 1.3 area %. The major light impurity was about 0.16 area % while the major heavy impurity exited the GC column immediately after 2-ethyl thiophene and accounted for about 1.2 % of the total area. Approximately 40 % of the 2-ethyl thiophene was removed as vapor degas at 140 °C, and the remainder of the chemical was used in the *PTx* measurements. The amount of the major light impurity in the material that was degassed at 140 °C was only 0.03 area %.

The cyclopropanecarbonitrile received from the committee contained about 0.37 mass % water. This water was effectively removed by Wiltec with molecular sieves prior to the phase equilibrium measurements.

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