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Vapor−Liquid Equilibrium Measurements on Three Binary Mixtures: Difluoromethane/Hydrogen Chloride, *cis*-1,3-Dichloropropene/*trans*-1,3-Dichloropropene, and Pyrrole/Water

W. Vincent Wilding,* Karen L. Adams, Alexander E. Carmichael, Jeffery B. Hull, Thomas C. Jarman, Kathy P. Jenkins, Tonya L. Marshall, and Howard L. Wilson

Department of Chemical Engineering, Brigham Young University, Provo, Utah 84602

Vapor−liquid equilibrium measurements using the PTx method have been made on three binary mixtures: difluoromethane/hydrogen chloride, *cis*-1,3-dichloropropene/*trans*-1,3-dichloropropene, and pyrrole/water. Each binary mixture was studied at two temperatures. Equilibrium vapor and liquid-phase compositions were derived from the PTx data using the Soave−Redlich−Kwong equation of state to represent the vapor phase and the NRTL activity coefficient model to represent the liquid phase. The pyrrole/water system exhibited a region of immiscibility at the lower temperature at which it was studied. Karl Fischer titration was used to determine the compositions of the equilibrium liquid phases.

Introduction

Experimental vapor−liquid equilibrium data are essential to process design and optimization. These measurements, sponsored by the Design Institute for Physical Properties (DIPPR) of the American Institute of Chemical Engineers (AIChE), provide accurate binary vapor−liquid equilibrium data on systems of industrial importance. Each system is studied at two temperatures to determine the temperature dependence of the activity coefficient model. The data are also useful for determining parameters for group contribution correlations. Table 1 shows the systems studied and the temperatures at which they were studied.

Experimental Section

Chemicals. The source and purities of the chemicals used in the measurements are given in Table 2.

The purities listed here are obtained from lot analyses reported by the manufacturer. The chemicals were degassed to remove any dissolved light contaminants. Degassing was performed by boiling off and discarding approximately 10% of the chemical. No further purification of these chemicals was performed.

Experimental Apparatus. An isothermal, binary PTx experiment consists of measuring the total pressure as a function of composition. Measurements are made across the entire composition range. By using an equation of state for vapor fugacity coefficients and an activity model for liquid-phase activity coefficients, the PTx data can be used to determine equilibrium phase compositions. Measurements are made at two temperatures to determine the temperature dependence of the activity coefficients.

Two different apparatuses were used for the PTx measurements. These are shown in Figures 1 and 2. The cell in Figure 1 was used for the low-pressure runs (both isotherms on system 2 and the lower temperature for system 3). This cell is made of thick-walled Pyrex with a Teflon cap and has an internal volume of approximately 300 cm^3. The cap screws into the cell and forms a seal with an O-ring. Small-bore tubing connected through the cap provide for the addition of components and degassing. A thermowell, into which a platinum resistance thermometer is inserted, also extends into the cell.

Table 1. Experimental Systems and Temperatures

system	isotherm, °C
1. difluoromethane/hydrogen chloride	−25, 0
2. *cis*-1.3-dichloropropene/ *trans*-1,3-dichloropropene	50, 100
3. pyrrole/water	75, 150

Table 2. Sources and Purities of Chemicals

substance	source	purity, mass %
difluoromethane	Solvay	99.50
hydrogen chloride	Matheson	100.00
cis-1,3-dichloropropene	Dow-Elanco	98.23
trans-1,3-dichloropropene	Dow-Elanco	97.93
pyrrole	Aldrich	99.70
water	Mallinckrodt	99.90

Increments of the compounds are charged to the cell using weighed syringes or flasks. Weights are accurate to ±0.001 g.

The platinum thermometer was calibrated using ice and steam points and was referenced to a NIST traceable standard. Temperatures in this apparatus were measured to an accuracy of ±0.1 K. During the course of a run, the temperature was held constant to within ±0.05 K.

The pressures were measured with a mercury manometer, which extends into the side of the cell. The manometer is connected to a McLeod gauge for cell pressures below

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* Corresponding author. E-mail: wildingv@byu.edu. Fax: (801) 378−7799.

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Table 3. Vapor Pressure Comparison

compound	t/°C	vapor pressure/kPa measd	 DIPPR 801	% dev (measd − lit.)/measd × 100
difluoromethane	−25	331.22	337.16	−1.79
	0	808.88	813.38	−0.56
hydrogen chloride	−25	1271.67	1253.30	1.44
	0	2606.67	2562.87	1.68
cis-1,3-dichloropropene	50	14.88		
	100	91.70		
trans-1,3-dichloropropene	50	10.54		
	100	69.79		
pyrrole	75	14.66	14.36	2.31
	150	182.5	178.61	2.13
water	75	38.6	38.56	0.10
	150	477.4	475.09	0.48

Table 4. Results of Vapor−Liquid Equilibrium Measurements by the PTx Method for the Difluoromethane (A)/Hydrogen Chloride (B) System at −25 °C[a]

run no.	mol % A			pressure/kPa		activity coeff		fugacity coeff		rel. volatility B/A
	charge	liquid	vapor	measd	calcd	A	B	A	B	
1	100.00	100.00	100.00	331.2	331.2	1.000	1.127	0.943	0.975	3.865
3	100.00	100.00	100.00	331.5	331.2	1.000	1.127	0.943	0.975	3.865
1	98.12	98.26	93.63	350.1	348.9	1.000	1.122	0.940	0.973	3.843
3	95.05	95.26	84.08	382.1	379.0	1.000	1.113	0.935	0.970	3.806
3	90.07	90.45	71.64	428.9	426.8	1.001	1.101	0.927	0.965	3.748
3	85.29	85.78	62.03	472.9	472.2	1.003	1.090	0.920	0.960	3.693
1	82.51	83.42	57.86	493.6	495.0	1.003	1.085	0.916	0.958	3.665
3	80.76	81.33	54.47	514.8	515.0	1.004	1.080	0.913	0.956	3.641
1	75.04	76.10	47.06	563.0	564.7	1.007	1.069	0.906	0.951	3.582
1	67.79	68.91	38.75	628.2	632.0	1.012	1.056	0.895	0.945	3.504
1	57.70	58.74	29.53	723.7	726.0	1.021	1.040	0.881	0.936	3.397
2	55.59	56.15	27.53	749.2	749.8	1.023	1.036	0.878	0.934	3.371
2	55.23	55.78	27.25	753.0	753.2	1.024	1.036	0.877	0.933	3.367
2	48.10	48.79	22.41	816.8	817.1	1.032	1.027	0.868	0.927	3.298
1	47.81	48.65	22.33	817.5	818.3	1.032	1.027	0.868	0.927	3.296
1	47.37	48.19	22.03	822.9	822.5	1.032	1.026	0.867	0.927	3.292
2	40.02	40.84	17.65	893.8	889.6	1.042	1.019	0.857	0.921	3.221
2	29.45	30.35	12.24	988.0	985.6	1.058	1.010	0.843	0.912	3.124
2	20.75	21.56	8.28	1072.6	1066.8	1.073	1.005	0.832	0.904	3.046
2	14.30	14.96	5.56	1133.4	1128.5	1.086	1.002	0.823	0.899	2.989
2	8.83	9.30	3.37	1188.4	1182.2	1.098	1.001	0.816	0.894	2.941
2	4.61	4.88	1.73	1230.0	1224.4	1.107	1.000	0.810	0.890	2.905
2	0.00	0.00	0.00	1271.7	1271.7	1.118	1.000	0.804	0.886	2.865

[a] NRTL parameters: $\tau_{12} = 0.2160$, $\tau_{21} = -0.0950$, and $\alpha = 0.2$.

Table 5. Results of Vapor−Liquid Equilibrium Measurements by the PTx Method for the Difluoromethane (A)/Hydrogen Chloride (B) System at 0 °C[a]

run no.	mol % A			pressure/kPa		activity coeff		fugacity coeff		rel. volatility B/A
	charge	liquid	vapor	measd	calcd	A	B	A	B	
1	100.00	100.00	100.00	811.1	809.1	1.000	1.069	0.895	0.955	2.874
3	100.00	100.00	100.00	809.1	809.1	1.000	1.069	0.895	0.955	2.874
1	98.12	98.33	95.35	841.1	838.4	1.000	1.067	0.891	0.953	2.866
3	95.05	95.37	87.83	891.7	890.5	1.000	1.065	0.885	0.948	2.852
3	90.07	90.64	77.40	974.9	973.7	1.000	1.061	0.875	0.941	2.828
3	85.29	86.04	68.74	1055.3	1054.8	1.001	1.058	0.865	0.935	2.804
1	82.51	83.92	65.15	1093.3	1092.3	1.001	1.056	0.860	0.932	2.792
3	80.76	81.64	61.54	1132.5	1132.7	1.001	1.054	0.856	0.928	2.780
1	75.04	76.73	54.51	1220.5	1219.9	1.003	1.050	0.845	0.922	2.752
1	67.79	69.60	45.80	1345.0	1346.5	1.005	1.044	0.831	0.912	2.710
1	57.70	59.41	35.62	1525.1	1528.0	1.010	1.035	0.811	0.899	2.646
2	55.59	56.48	33.07	1578.2	1580.2	1.011	1.032	0.805	0.895	2.627
2	55.23	56.10	32.75	1586.5	1587.0	1.012	1.032	0.804	0.894	2.624
2	48.10	49.23	27.34	1710.5	1709.6	1.017	1.026	0.791	0.886	2.577
1	47.81	49.21	27.33	1706.3	1709.9	1.017	1.026	0.791	0.885	2.577
1	47.37	48.72	26.97	1716.9	1718.6	1.017	1.026	0.790	0.885	2.574
2	40.02	41.40	21.89	1851.5	1849.6	1.024	1.020	0.776	0.876	2.521
2	29.45	31.01	15.55	2038.5	2036.1	1.038	1.012	0.757	0.862	2.442
2	20.75	22.18	10.73	2200.3	2195.8	1.054	1.007	0.740	0.851	2.370
2	14.30	15.48	7.33	2322.8	2318.3	1.068	1.003	0.728	0.843	2.313
2	8.83	9.66	4.51	2429.6	2425.6	1.083	1.001	0.717	0.835	2.262
2	4.61	5.09	2.36	2514.2	2511.1	1.097	1.000	0.709	0.829	2.221
2	0.00	0.00	0.00	2607.4	2607.4	1.114	1.000	0.699	0.823	2.173

[a] NRTL parameters: $\tau_{12} = -0.6445$, $\tau_{21} = 0.8410$, and $\alpha = 0.2$.

about 50 kPa, or it is open to room pressure for higher pressures. The mercury levels in the cell manometer were read with a cathetometer to an accuracy of ±0.05 kPa. Atmospheric pressure was measured with a barometer

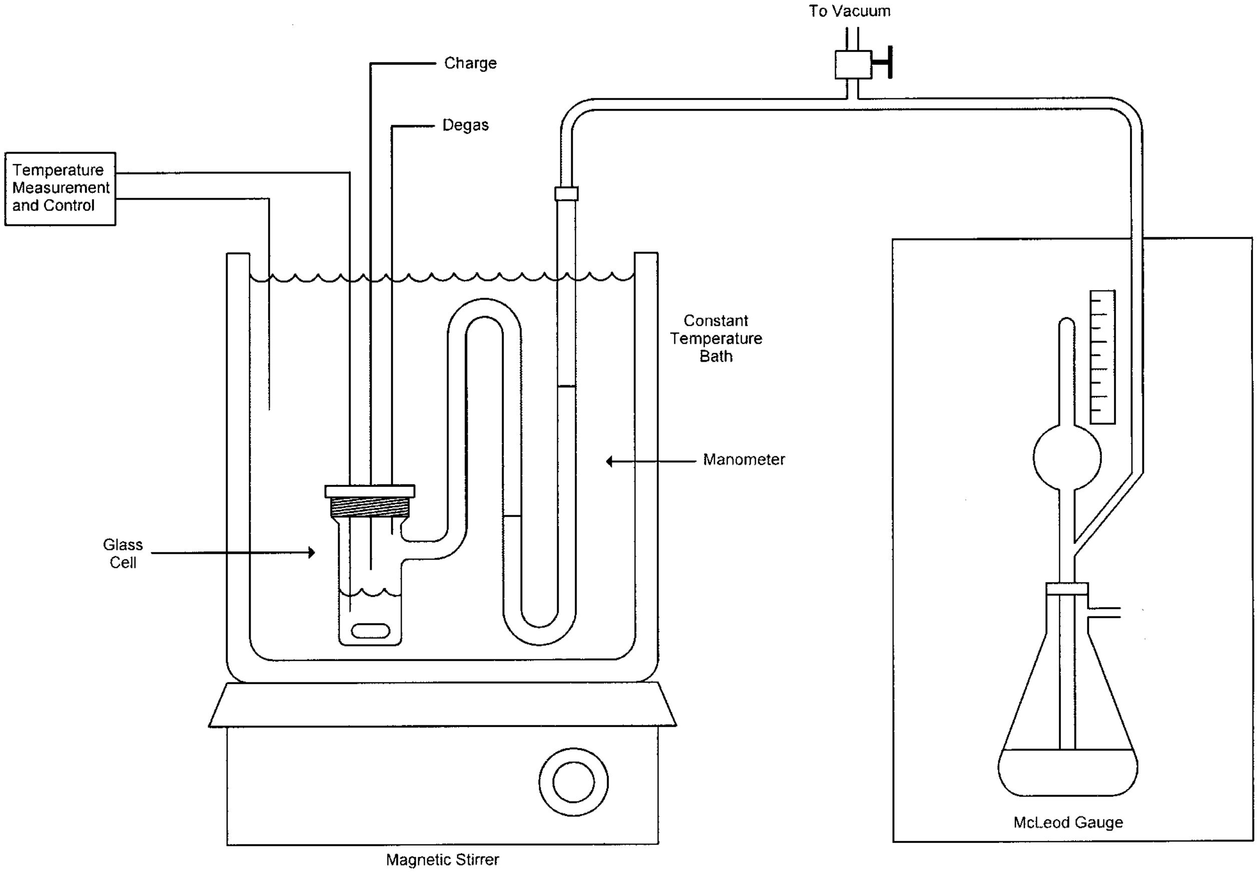

Figure 1. Glass PTx apparatus.

located adjacent to the experimental apparatus. Measured pressures were corrected for the temperature dependence of the density of mercury and for the vapor pressure of mercury.

The apparatus shown in Figure 2 was used for the high-pressure runs (both isotherms on system 1 and the higher isotherm on system 3). This apparatus consists of a 300 cm^3 stainless steel cell with connections for pressure measurement and for charging components or degassing. A thermowell, into which a platinum resistance thermometer is inserted, also extends into the cell. The temperature was measured with the same platinum thermometer as used in the glass apparatus. The pressure was measured with a Paroscientific pressure transducer accurate to approximately ±0.05 kPa.

The liquid−liquid equilibrium measurement on the lower isotherm of the pyrrole/water system was performed by drawing samples of the equilibrium phases and analyzing these with a Mettler DL18 Karl Fischer titrator.

Experimental Procedure. In the PTx method, the entire composition range is traversed at each temperature. This requires at least two runs. To initiate the first run, the cell was charged with a weighed amount of one component. The cell contents were then degassed by removing vapor into a weighed, evacuated cell or a weighed syringe fitted with a valve. The cell contents were stirred with the magnetic stirrer (or shaken in the case of the stainless steel apparatus) until equilibrium was attained, and the pure component vapor pressure was measured. The cell contents were again degassed, and the pressure was measured. This process was repeated until the vapor pressure no longer changes upon further degassing. Thus, the measured pressure is an accurate pure-component vapor pressure.

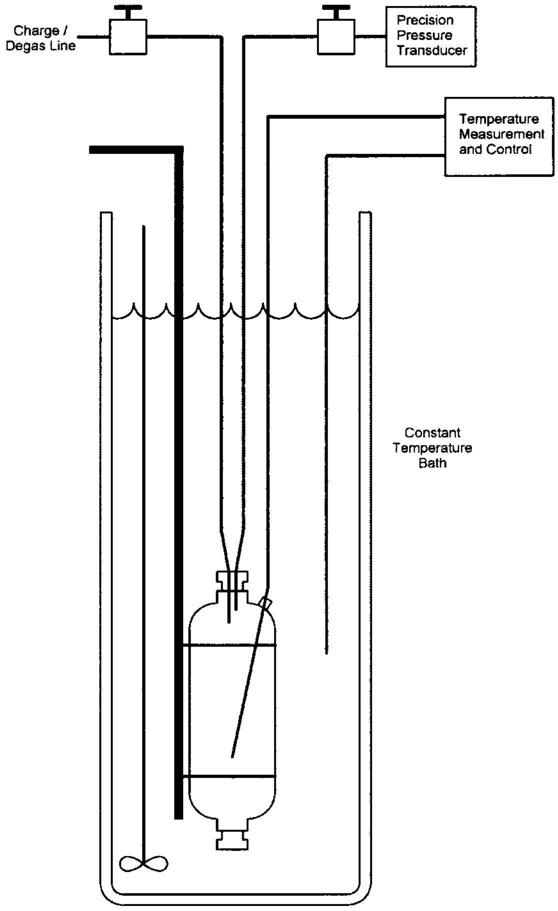

Figure 2. High-pressure stainless steel PTx apparatus.

Table 6. Results of Vapor−Liquid Equilibrium Measurements by the PTx Method for the *trans*-1,3-Dichloropropene (A)/*cis*-1,3-Dichloropropene (B) System at 50 °C[a]

run	mol % A			pressure/kPa		activity coeff		fugacity coeff		rel. volatility
no.	charge	liquid	vapor	measd	calcd	A	B	A	B	B/A
2	100.00	100.00	100.00	10.54	10.54	1.000	1.010	0.995	0.995	1.423
2	94.96	94.96	92.99	10.78	10.76	1.000	1.009	0.995	0.995	1.421
2	89.20	89.21	85.34	11.03	11.02	1.000	1.008	0.995	0.995	1.420
2	84.12	84.13	78.89	11.26	11.24	1.000	1.007	0.995	0.995	1.419
2	78.50	78.51	72.05	11.48	11.49	1.000	1.006	0.995	0.995	1.417
2	69.30	69.31	61.49	11.83	11.90	1.001	1.005	0.994	0.995	1.415
2	60.50	60.51	52.04	12.24	12.28	1.001	1.004	0.994	0.995	1.412
1	53.62	53.63	45.05	12.60	12.58	1.002	1.003	0.994	0.994	1.410
2	49.57	49.58	41.10	12.78	12.76	1.002	1.003	0.994	0.994	1.409
1	44.26	44.27	36.07	13.12	12.99	1.003	1.002	0.994	0.994	1.408
2	38.86	38.87	31.13	13.24	13.22	1.004	1.002	0.994	0.994	1.406
1	34.85	34.86	27.58	13.41	13.39	1.004	1.001	0.994	0.994	1.405
2	29.81	29.81	23.23	13.62	13.61	1.005	1.001	0.994	0.994	1.404
1	26.53	26.54	20.48	13.71	13.75	1.005	1.001	0.994	0.994	1.403
1	19.10	19.10	14.43	14.00	14.07	1.007	1.000	0.993	0.994	1.400
1	14.67	14.67	10.94	14.22	14.26	1.007	1.000	0.993	0.994	1.399
1	9.79	9.80	7.21	14.42	14.47	1.008	1.000	0.993	0.994	1.398
1	5.66	5.67	4.12	14.60	14.64	1.009	1.000	0.993	0.994	1.396
1	0.00	0.00	0.00	14.88	14.88	1.010	1.000	0.993	0.993	1.394

[a] NRTL parameters: $\tau_{12} = -0.1680$, $\tau_{21} = 0.1841$, and $\alpha = 0.2$.

Table 7. Results of Vapor−Liquid Equilibrium Measurements by the PTx Method for the *trans*-1,3-Dichloropropene (A)/*cis*-1,3-Dichloropropene (B) System at 100 °C[a]

run	mol % A			pressure/kPa		activity coeff		fugacity coeff		rel. volatility
no.	charge	liquid	vapor	measd	calcd	A	B	A	B	B/A
2	100.00	100.00	100.00	69.79	69.79	1.000	1.027	0.978	0.979	1.340
2	94.55	94.56	92.88	70.98	71.09	1.000	1.022	0.978	0.979	1.333
2	89.54	89.56	86.60	72.16	72.27	1.000	1.018	0.977	0.978	1.328
2	81.95	81.99	77.52	74.32	74.01	1.001	1.014	0.977	0.978	1.320
2	73.49	73.53	67.90	75.64	75.92	1.002	1.009	0.976	0.977	1.313
2	63.15	63.19	56.79	78.13	78.20	1.004	1.006	0.975	0.977	1.306
1	59.10	59.13	52.60	79.34	79.09	1.005	1.005	0.975	0.976	1.304
2	54.49	54.53	47.96	80.12	80.09	1.006	1.003	0.975	0.976	1.301
1	47.89	47.93	41.48	81.55	81.51	1.007	1.002	0.974	0.976	1.298
2	44.33	44.36	38.08	82.20	82.27	1.007	1.002	0.974	0.976	1.297
1	36.83	36.88	31.10	83.94	83.87	1.009	1.001	0.974	0.975	1.294
1	26.21	26.26	21.61	86.08	86.13	1.010	1.000	0.973	0.974	1.292
1	17.90	17.93	14.48	87.78	87.89	1.011	1.000	0.972	0.974	1.290
1	9.65	9.67	7.67	89.67	89.65	1.011	1.000	0.972	0.973	1.289
1	5.29	5.30	4.16	90.52	90.57	1.011	1.000	0.971	0.973	1.289
1	0.00	0.00	0.00	91.70	91.70	1.011	1.000	0.971	0.973	1.289

[a] NRTL parameters: $\tau_{12} = 0.6964$, $\tau_{21} = -0.5946$, and $\alpha = 0.2$.

After the pure component vapor pressure was measured, weighed increments of the second component were charged to the cell. After each increment, the cell contents were again degassed and allowed to equilibrate before the pressure was measured. Increments of the second component were added until over half of the composition range had been traversed. The cell was then emptied and cleaned in preparation for the second run.

The second run was 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 are designed to overlap in the midcomposition range to check for consistency between the runs.

Data Reduction Procedure. The PTx measurements result in data for total pressure as a function of charge composition at constant temperature. Using these values, equilibrium phase compositions and activity and fugacity coefficients were then calculated, with the Soave−Redlich−Kwong[1] equation of state representing the vapor phase and the NRTL activity coefficient model[2] representing the liquid phase. The critical constants, acentric factors,

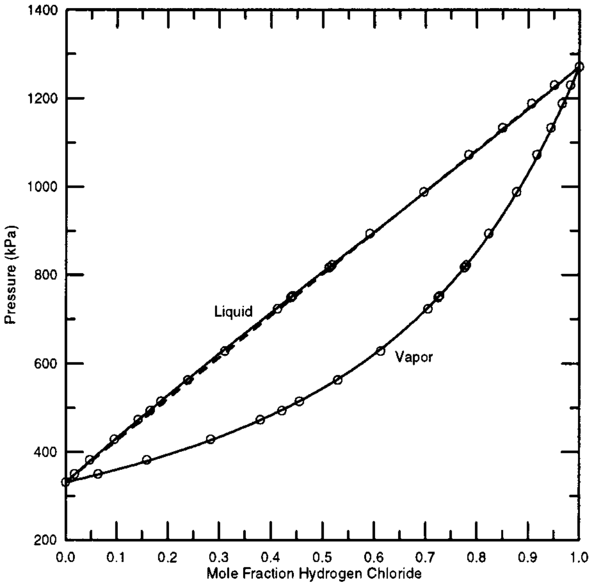

Figure 3. PTx results for the difluoromethane/hydrogen chloride system at −25 °C.

Table 8. Results of Vapor−Liquid Equilibrium Measurements by the PTx Method for the Pyrrole (A)/Water (B) System at 75 °C[a]

run	mol % A			pressure/kPa		activity coeff		fugacity coeff		rel. volatility
no.	charge	liquid	vapor	measd	calcd	A	B	A	B	B/A
2	100.00	100.00	100.00	14.66	14.66	1.000	7.640	0.995	1.000	20.036
2	97.84	97.87	70.69	20.97	20.34	1.001	7.259	0.994	0.999	19.009
2	95.59	95.64	54.95	30.98	25.66	1.002	6.882	0.992	0.998	17.972
2	90.98	91.05	38.94	35.16	34.83	1.010	6.164	0.990	0.997	15.948
2	81.08	81.17	26.31	46.38	47.94	1.050	4.861	0.987	0.995	12.074
	78.63	78.71[b]	24.86	50.13	50.13	1.066	4.581	0.987	0.995	11.058
	3.18	3.10[c]	24.86	50.13	50.13	27.061	1.006	0.986	0.995	0.097
1	2.00	1.95	19.23	46.35	46.98	31.375	1.003	0.987	0.995	0.083
1	0.00	0.00	0.00	38.57	38.57	40.882	1.000	0.990	0.996	0.064

[a] NRTL parameters: $\tau_{12} = 0.3075$, $\tau_{21} = 3.422$, and $\alpha = 0.2$. [b] This point is within the two-liquid-phase region. The liquid composition is the composition of the pyrrole-rich phase. The activity coefficients and relative volatility for this data point were calculated using the composition of this phase. [c] This point is within the two-liquid-phase region. The liquid composition is the composition of the Water-rich phase. The activity coefficients and relative volatility for this data point were calculated using the composition of this phase.

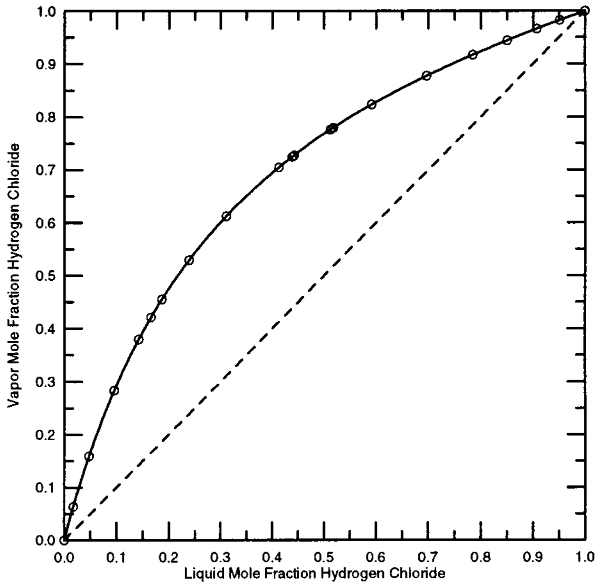

Figure 4. *y*−*x* Plot for the difluoromethane/hydrogen chloride system at −25 °C.

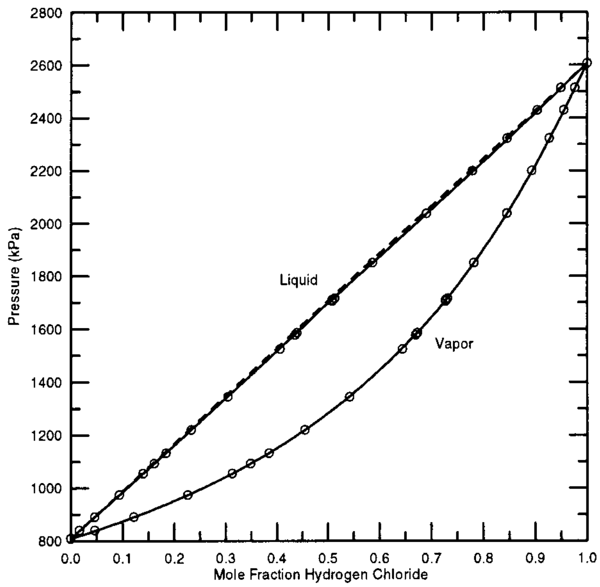

Figure 6. PTx results for the difluoromethane/hydrogen chloride system at 0 °C.

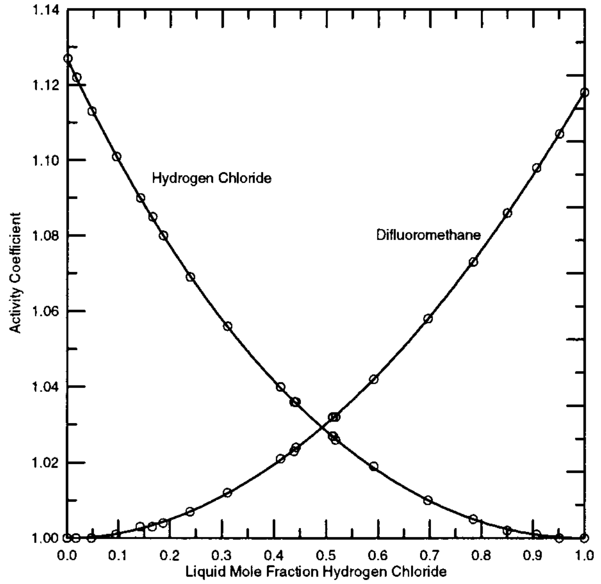

Figure 5. Activity coefficients for the difluoromethane/hydrogen chloride system at −25 °C.

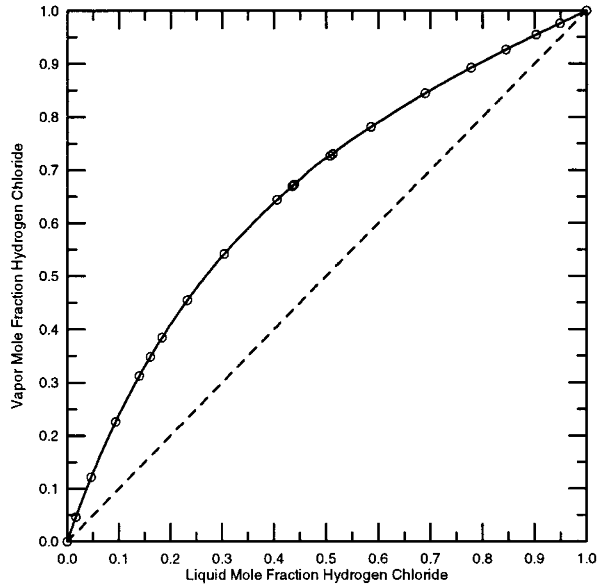

Figure 7. Y-X plot for the difluoromethane/hydrogen chloride system at 0 °C.

and liquid densities used in the data reduction procedure were taken from the DIPPR 801 database.[3] The Soave equation binary interaction parameters were assumed to be zero.

Table 9. Results of Vapor–Liquid Equilibrium Measurements by the PTx Method for the Pyrrole (A)/Water (B) System at 150 °C[a]

run	mol % A			pressure/kPa		activity coeff		fugacity coeff		rel. volatility
no.	charge	liquid	vapor	measd	calcd	A	B	A	B	B/A
2	100.00	100.00	100.00	182.5	182.5	1.000	3.633	0.966	0.997	9.251
2	96.82	97.10	78.95	237.3	226.6	1.000	3.520	0.958	0.993	8.918
2	91.65	92.28	58.87	298.0	293.4	1.004	3.331	0.948	0.987	8.357
2	87.18	88.04	48.38	343.8	345.8	1.009	3.166	0.940	0.983	7.857
2	79.73	80.78	37.55	418.0	421.5	1.027	2.886	0.929	0.978	6.990
2	69.78	70.83	29.53	493.0	497.5	1.073	2.518	0.918	0.973	5.792
2	60.34	61.20	25.33	536.1	543.7	1.155	2.185	0.912	0.970	4.650
2	50.23	50.80	22.91	562.1	569.3	1.312	1.860	0.909	0.968	3.475
1	41.71	41.80	22.00	575.7	577.2	1.551	1.612	0.908	0.968	2.547
2	40.43	40.74	21.95	573.4	577.5	1.588	1.585	0.908	0.968	2.445
1	30.90	30.98	21.96	580.3	577.7	2.090	1.361	0.908	0.968	1.595
2	29.72	29.81	22.01	577.3	577.6	2.177	1.337	0.908	0.968	1.505
1	20.30	20.28	22.47	580.3	577.0	3.264	1.169	0.908	0.968	0.878
2	18.96	18.94	22.50	577.1	577.1	3.499	1.150	0.908	0.968	0.805
1	9.52	9.36	20.70	572.3	570.9	6.459	1.041	0.910	0.968	0.395
1	5.15	5.00	16.33	561.7	551.1	9.265	1.012	0.914	0.969	0.269
1	2.64	2.53	10.86	539.7	525.2	11.682	1.003	0.920	0.970	0.213
1	0.00	0.00	0.00	477.5	477.5	15.170	1.000	0.931	0.972	0.165

[a] NRTL parameters: $\tau_{12} = -0.3845$, $\tau_{21} = 3.135$, and $\alpha = 0.2$.

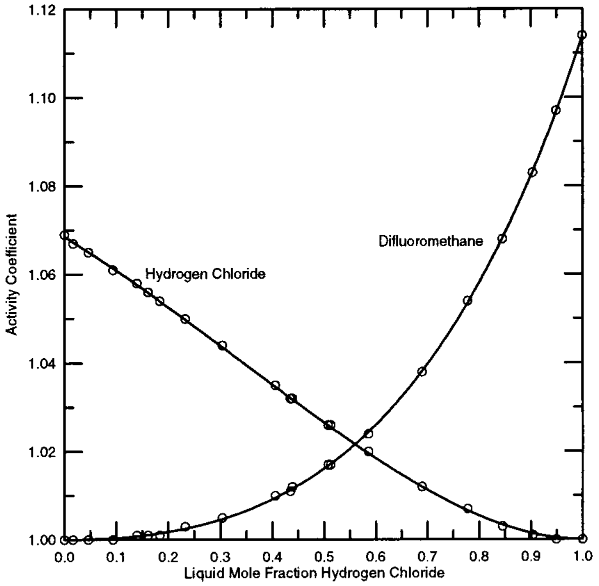

Figure 8. Activity coefficients for the difluoromethane/hydrogen chloride system at 0 °C.

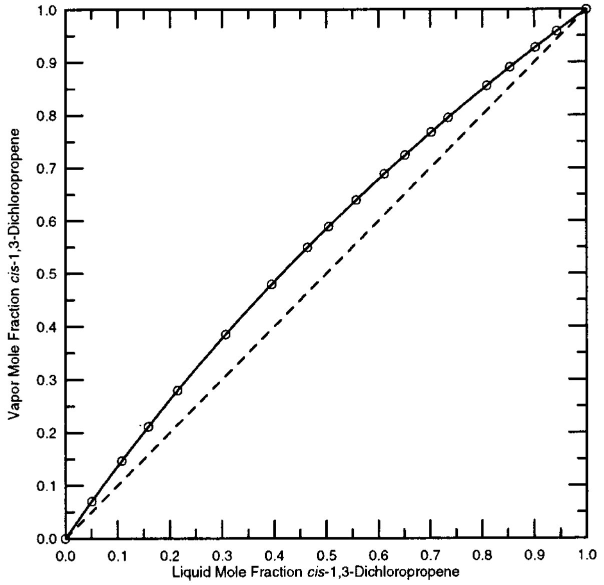

Figure 10. *y*–*x* Plot for the *trans*-1,3-dichloropropene/*cis*-1,3-dichloropropene system at 50 °C.

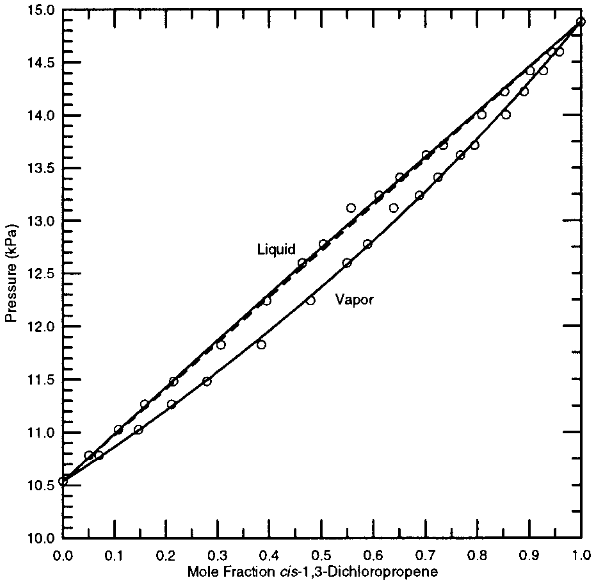

Figure 9. PTx results for the *trans*-1,3-dichloropropene/*cis*-1,3-dichloropropene system at 50 °C.

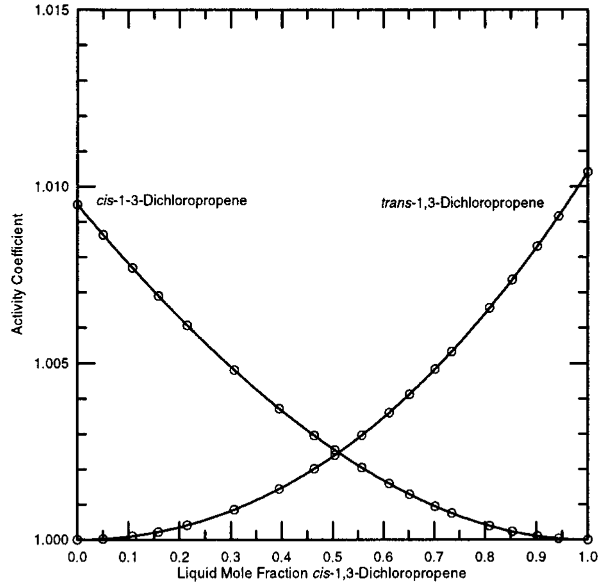

Figure 11. Activity coefficients for the *trans*-1,3-dichloropropene/*cis*-1,3-dichloropropene system at 50 °C.

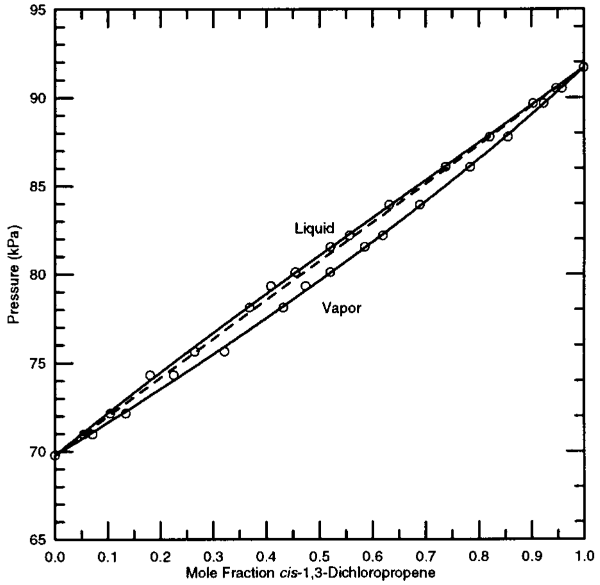

Figure 12. PTx results for the *trans*-1,3-dichloropropene/*cis*-1,3-dichloropropene system at 100 °C.

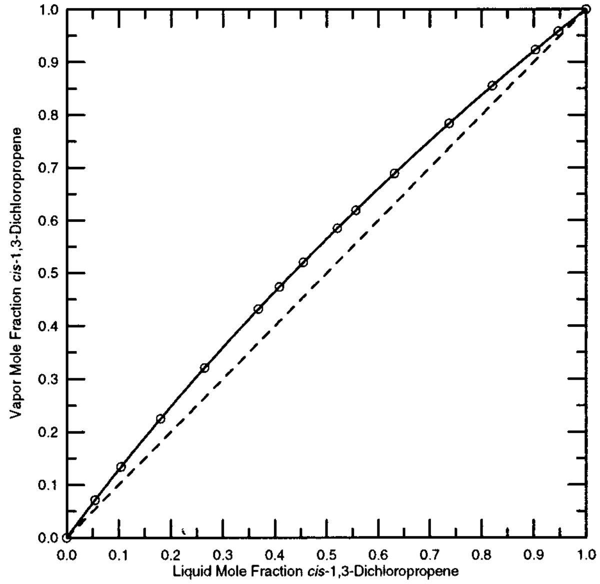

Figure 13. $y-x$ plot for the *trans*-1,3-dichloropropene/*cis*-1,3-dichloropropene system at 100 °C.

To derive equilibrium phase compositions from PTx data, an iterative process was used to solve the fundamental equation of vapor–liquid equilibrium shown in eq 1, where

$$y_i\phi_i P = x_i\gamma_i P_i^{\rm o}\phi_i^{\rm o}\exp\left[\left(\frac{\bar{V}_i}{RT}\right)(P - P_i^{\rm o})\right] \tag{1}$$

y_i is the vapor mole fraction of the component i, n_i is the fugacity coefficient of component i in the vapor phase, P is the total pressure, $x_{\rm i}$ is the liquid mole fraction of component i, γ_i is the activity coefficient of component i, $P_i^{\rm o}$ is the vapor pressure of pure component i at system temperature, $\varphi_i^{\rm o}$ is the fugacity coefficient of pure component i at system temperature and corresponding vapor pressure of pure i, and the exponential term is the Poynting correction in which $\bar{V}_i$ is the liquid molar volume of component i. This volume is calculated from pure component density data from the literature adjusted to the temperature of the measurements using the Rackett equation.

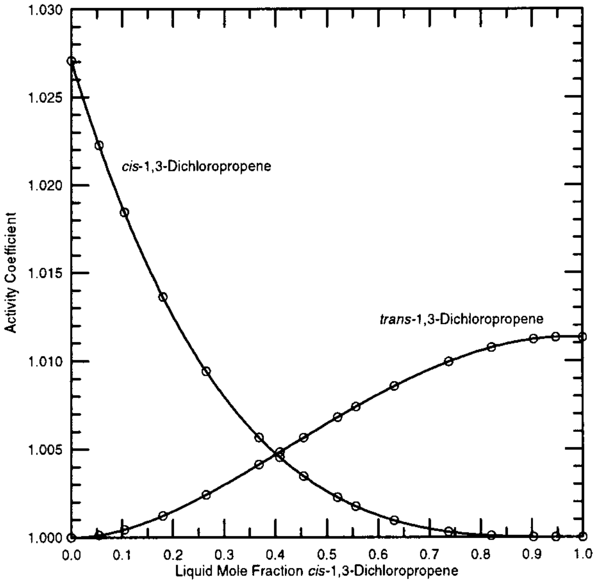

Figure 14. Activity coefficients for the *trans*-1,3-dichloropropene/*cis*-1,3-dichloropropene system at 100 °C.

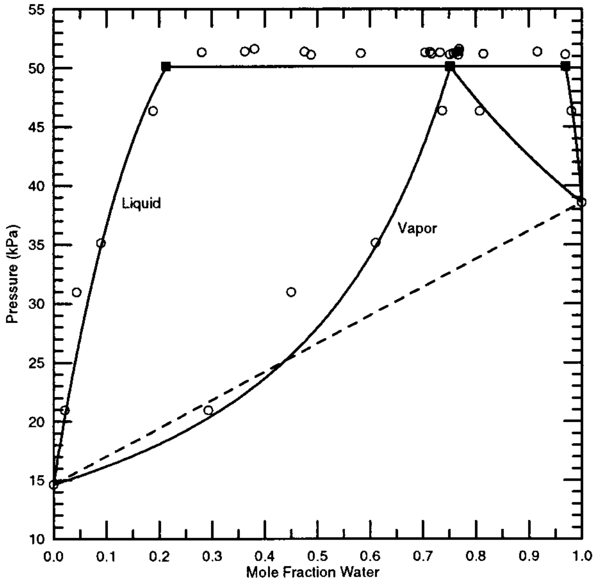

Figure 15. PTx results for the pyrrole/water system at 75 °C.

The data reduction procedure consists of fitting the pressure data to eq 1 across the entire composition range by adjusting the parameters of the activity coefficient model. The NRTL equations (eq 2) were used in the data reduction procedure:

$$\ln(\gamma_1) = {x_2}^2\left[\frac{\tau_{21}{G_{21}}^2}{(x_1 + x_2{G_{21}}^2)} + \frac{\tau_{12}G_{12}}{(x_2 + x_1{G_{12}}^2)}\right],$$

$$\ln(\gamma_2) = {x_1}^2\left[\frac{\tau_{12}{G_{12}}^2}{(x_2 + x_1G_{12})^2} + \frac{\tau_{21}G_{21}}{(x_1 + x_2\,G_{21})^2}\right] \tag{2}$$

$$G_{21} = \exp(-\alpha\tau_{21}), \quad G_{12} = \exp(-\alpha\tau_{12})$$

where γ_1 and γ_2 are activity coefficients, x_1 and x_2 are component liquid mole fractions, and α, τ_{12}, and τ_{21} are experimentally determined parameters.

To begin the data reduction procedure, the ideal-solution parameters of the activity coefficient model are selected. Then, assuming the liquid composition is the same as the

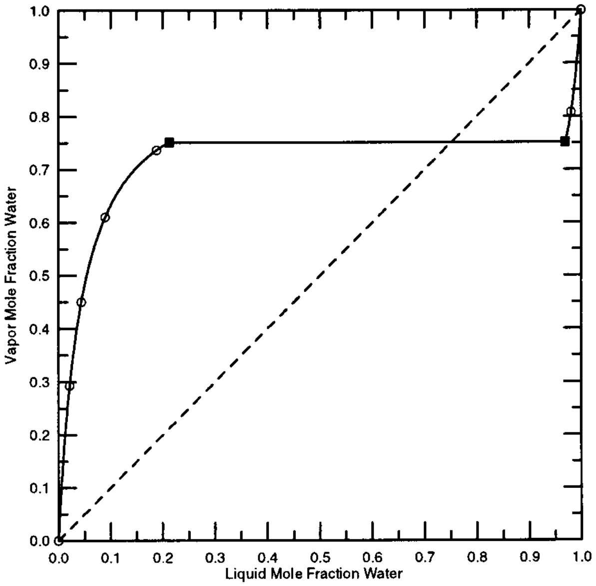

Figure 16. Y-X plot for the pyrrole/water system at 75 °C.

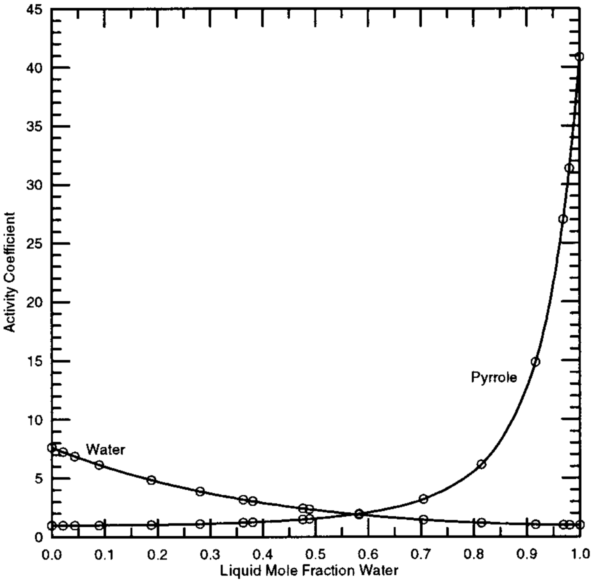

Figure 17. Activity coefficients for the pyrrole/water system at 75 °C.

charge composition and the fugacity coefficients are unity, eq 1 is solved for the product Py_i for each component. The calculated pressure is then the sum of these products:

$$P_{\text{calc}} = \sum Py_i \tag{3}$$

The vapor mole fraction for each component is then determined by

$$y_i = \frac{(Py_i)}{P_{\text{calc}}} \tag{4}$$

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

The next step is 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 converges. As part of each iteration step, the amount of material taken out of the cell during degassing is subtracted from the total charge at the calculated vapor composition.

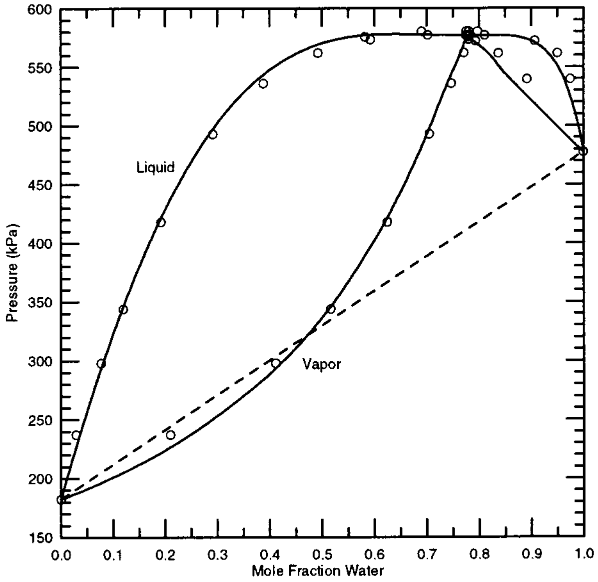

Figure 18. PTx results for the pyrrole/water system at 150 °C.

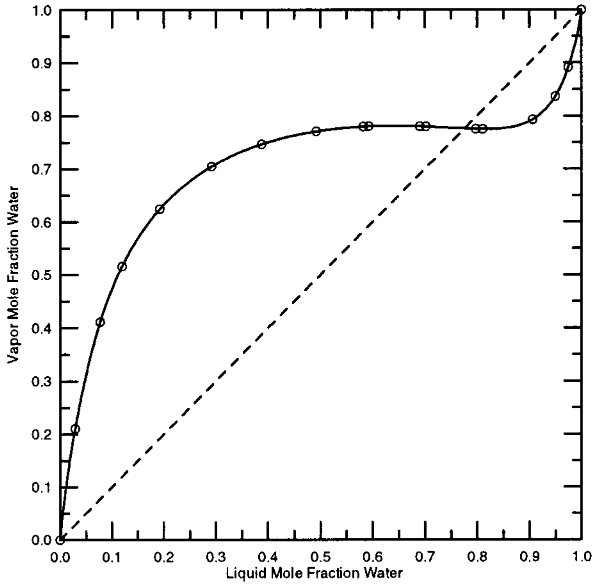

Figure 19. $y-x$ plot for the pyrrole/water system at 150 °C.

This procedure is performed for each point across the composition range. The calculated pressures are compared to the measured pressures and the activity coefficient parameters are adjusted to find the best fit of the total pressure data.

Results and Discussion

The PTx measurements include pure-component vapor pressures. Table 3 compares these measured vapor pressures with values calculated from the vapor pressure correlations given in the DIPPR 801 database for each component at each isotherm.

Difluoromethane/Hydrogen Chloride. Tables 4 and 5 give the results of the PTx measurements on the difluoromethane/hydrogen chloride system at −25 and 0 °C. A slight positive deviation from Raoult's law is exhibited at both temperatures. The NRTL equation parameters used to correlate the data are given at the bottom of each table.

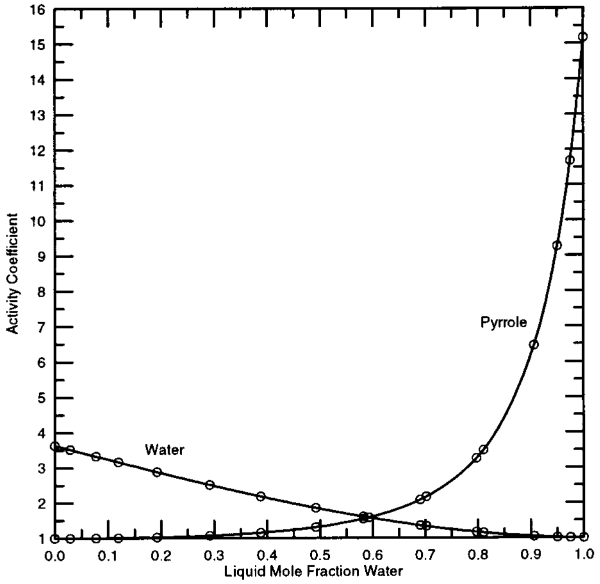

Figure 20. Activity coefficients for the pyrrole/water system at 150 °C.

Figure 3 shows the measured data and the total-pressure correlation at −25 °C, and Figures 4 and 5 show the derived $y-x$ and activity coefficient plots, respectively. Figure 6 is the total-pressure plot for the measurements at 0 °C, and Figures 7 and 8 show the derived $y-x$ and activity coefficient plots for these data.

trans-1,3-Dichloropropene/cis-1,3-Dichloropropene. Tables 6 and 7 present the results for the *trans*-1,3-dichloropropene/*cis*-1,3-dichloropropene system at 50 and 100 °C. These chemicals were supplied by the DIPPR 805 committee at the highest purity available. No further purification was possible. Due to the structural similarity of these compounds nearly ideal behavior is exhibited at both temperatures. However, the cis isomer has significantly higher vapor pressures than the trans isomer. The 50 °C results are shown in Figures 9−11, and the 100 °C results are shown in Figures 12−14.

Pyrrole/Water. Tables 8 and 9 present the results for the pyrrole/water system at 75 and 150 °C. Large positive deviations from Raoult's law are exhibited at both temperatures. At 75 °C, a large immiscibility exists with the composition limits of 0.031 and 0.787 mol fraction of pyrrole. These compositions were determined separately from the PTx measurements using Karl Fischer titration. The results at 75 °C are shown in Figures 15−17. At 150 °C there is no immiscibility, but a minimum boiling azeotrope occurs at a composition of about 0.22 mol fraction of pyrrole. The compositions of these endpoints were used to calculate the NRTL parameters for this system.[4] The 150 °C results are shown in Figures 18−20.

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