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Phase Equilibria on Eight Binary Mixtures

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Vapor−liquid equilibria are reported for the following five systems at two temperatures each: 2-(2-(hexyloxy)ethoxy)ethanol + 1,2-ethanediol; 2-(hexyloxy)ethanol + 1,2-propanediol; acetone cyanohydrin + acetone; acetone cyanohydrin + hydrogen cyanide; propyl mercaptan + butane. 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 Wilson or the van Laar activity coefficient model to represent the liquid phase. The solubility of oxygen in propylene oxide, nitrogen in propylene oxide, and methane in dichloromethane has been measured at three pressures at each of two or three temperatures.

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 805/94 to obtain phase equilibrium data on eight binary systems. These systems and their measurements conditions follow:

1. 2-(2-(hexyloxy)ethoxy)ethanol + 1,2-ethanediol at 100 and 180 °C
2. 2-(hexyloxy)ethanol + 1,2-propanediol at 100 and 180 °C
3. acetone cyanohydrin + acetone at 20 and 75 °C
4. acetone cyanohydrin + hydrogen cyanide at 15 and 75 °C
5. propyl mercaptan + butane at 70 and 110 °C
6. propylene oxide + oxygen at 25 and 100 °C
7. propylene oxide + nitrogen at 25 and 100 °C
8. dichloromethane + methane at −30, 0, and 30 °C

Vapor−liquid equilibria (VLE) were determined 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. Solubility data were obtained by directly measuring the amount of gas in the liquid at three pressures at each temperature. The composition of the vapor phase was determined using an equation of state.

Experimental Section

The apparatus and procedures used for the *PTx* measurements have been described earlier (Giles et al., 1996). Temperatures were measured with platinum resistance thermometers that were calibrated using ice and steam points and referenced to an NIST traceable standard resistance thermometer using the ITS-90 temperature scale. Temperatures were measured with a precision of ±0.01 K and an accuracy of ±0.05 K or better.

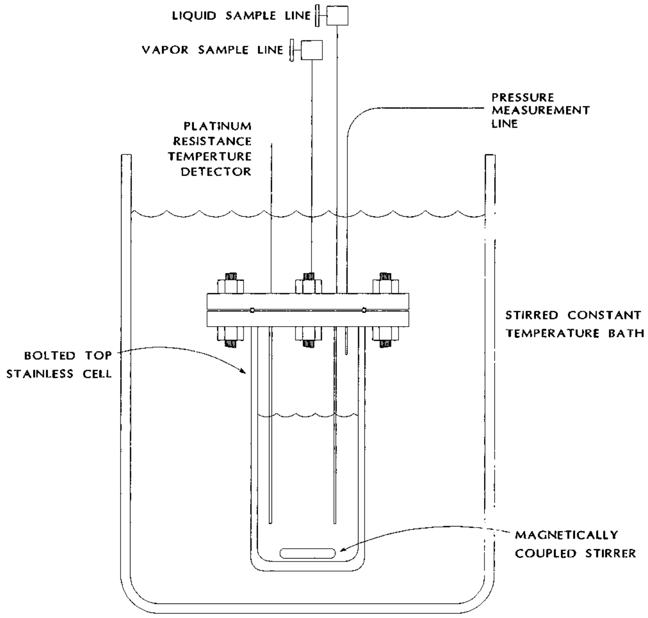

Figure 1. Bolted-top cell apparatus.

Measurements were performed in a glass still apparatus for systems 1 and 2. The pure-component vapor pressure of acetone cyanohydrin for systems 3 and 4 was also measured with this apparatus. Pressures measured using this apparatus are estimated to be accurate to within ±0.025 kPa.

PTx data for the 20 °C isotherm and for the lower half of the 75 °C isotherm of system 3 were measured using a glass cell apparatus. Pressures measured using this apparatus are estimated to be accurate to within ±0.05 kPa. The upper half of the 75 °C isotherm of system 3 as well as both isotherms of systems 4 and 5 were measured using a stainless steel apparatus. The pressure was measured to within ±0.05 kPa using a mercury manometer for the 15 °C isotherm of system 4. The pressure was measured with a calibrated pressure transducer with an estimated accuracy of ±0.5 kPa for the other systems studied using this apparatus.

The solubility measurements for systems 6−8 were performed in the apparatus shown in Figure 1. This apparatus consisted of a 2 L bolted-top cell in a constant temperature bath. Lines extended from the cell for sampling the liquid and vapor phases, adding material, and

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Table 1. *PTx* Measurement Results on 2-(2-(Hexyloxy)ethoxy)ethanol (A) + 1,2-Ethanediol (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 = 100 °C[a]												
1	100.00	100.00	100.00	0.25	0.25	1.000	2.446	1.000	1.000	1.0000	1.0000	20.796
1	97.47	97.48	65.54	0.36	0.37	1.000	2.391	0.999	1.000	1.0000	1.0000	20.323
1	94.81	94.82	48.01	0.49	0.49	1.001	2.334	0.999	1.000	1.0000	1.0000	19.822
1	89.59	89.60	31.39	0.72	0.71	1.005	2.227	0.999	1.000	1.0000	1.0000	18.831
1	79.59	79.61	18.76	1.10	1.08	1.022	2.034	0.998	1.000	1.0001	1.0000	16.907
1	69.29	69.32	13.18	1.40	1.38	1.056	1.850	0.998	1.000	1.0001	1.0000	14.885
1	59.69	59.71	10.26	1.62	1.61	1.109	1.693	0.998	0.999	1.0001	1.0000	12.961
1	49.93	49.94	8.34	1.78	1.79	1.196	1.545	0.998	0.999	1.0001	1.0000	10.969
2	41.03	41.04	7.09	1.90	1.91	1.323	1.421	0.997	0.999	1.0001	1.0000	9.119
1	39.35	39.36	6.89	1.91	1.93	1.355	1.399	0.997	0.999	1.0001	1.0000	8.768
2	30.63	30.63	6.00	2.01	2.01	1.581	1.289	0.997	0.999	1.0001	1.0000	6.922
2	19.80	19.80	5.10	2.09	2.08	2.149	1.164	0.997	0.999	1.0001	1.0000	4.598
2	9.89	9.89	4.27	2.12	2.12	3.668	1.064	0.997	0.999	1.0001	1.0000	2.463
2	4.93	4.93	3.52	2.13	2.13	6.110	1.023	0.997	0.999	1.0001	1.0000	1.422
2	2.26	2.26	2.53	2.13	2.14	9.596	1.006	0.997	0.999	1.0001	1.0000	0.890
2	0.00	0.00	0.00	2.12	2.12	17.704	1.000	0.997	0.999	1.0001	1.0000	0.480
t = 180 °C[b]												
1	100.00	100.00	100.00	9.81	9.81	1.000	2.095	0.989	1.002	1.0000	0.9992	12.401
1	96.98	97.09	73.35	12.48	13.03	1.000	2.055	0.986	1.000	1.0002	0.9992	12.139
1	94.56	94.75	60.21	15.17	15.53	1.001	2.022	0.984	0.999	1.0003	0.9993	11.925
1	90.04	90.35	44.85	20.05	20.01	1.003	1.962	0.981	0.998	1.0006	0.9994	11.518
1	79.86	80.32	27.89	29.75	29.16	1.016	1.829	0.974	0.995	1.0012	0.9995	10.558
1	70.25	70.74	20.13	37.14	36.59	1.039	1.706	0.969	0.994	1.0016	0.9996	9.592
1	60.88	61.33	15.58	42.98	42.69	1.078	1.590	0.966	0.992	1.0020	0.9997	8.593
1	50.88	51.24	12.35	47.98	48.01	1.146	1.470	0.962	0.991	1.0023	0.9998	7.455
2	42.88	43.06	10.45	51.62	51.44	1.233	1.377	0.961	0.991	1.0025	0.9999	6.479
1	40.90	41.15	10.07	52.05	52.14	1.260	1.356	0.960	0.990	1.0025	0.9999	6.243
2	31.73	31.91	8.47	54.83	54.98	1.439	1.257	0.959	0.990	1.0027	0.9999	5.062
1	29.66	29.78	8.15	55.07	55.52	1.497	1.235	0.958	0.990	1.0027	0.9999	4.780
2	20.36	20.48	6.85	57.12	57.41	1.890	1.143	0.957	0.989	1.0029	1.0000	3.502
2	10.10	10.16	5.32	58.86	58.81	3.031	1.053	0.957	0.989	1.0029	1.0000	2.012
2	4.81	4.82	3.93	58.98	59.27	4.756	1.017	0.957	0.989	1.0030	1.0000	1.238
2	2.60	2.60	2.80	59.13	59.32	6.301	1.006	0.958	0.989	1.0030	1.0000	0.925
2	0.00	0.00	0.00	58.85	58.85	10.001	1.000	0.959	0.989	1.0029	1.0000	0.580

[a] Wilson equation parameters: $\Lambda_{AB} = 0.0535$, $\Lambda_{BA} = 1.0535$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.0823$, $\Lambda_{BA} = 1.1950$.

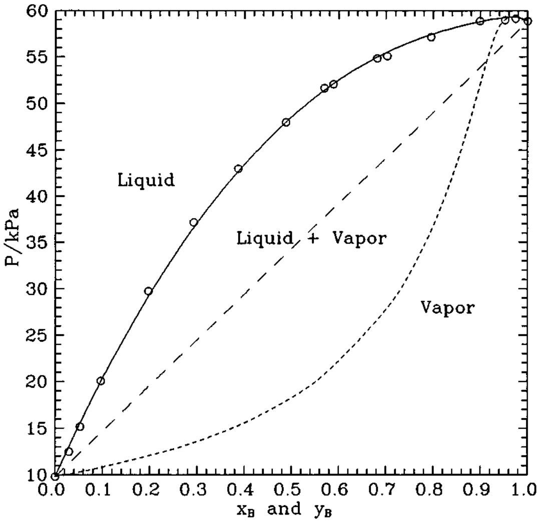

Figure 2. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (— —) for 2-(2-(hexyloxy)ethoxy)ethanol (A) + 1,2-ethanediol (B) at 180 °C.

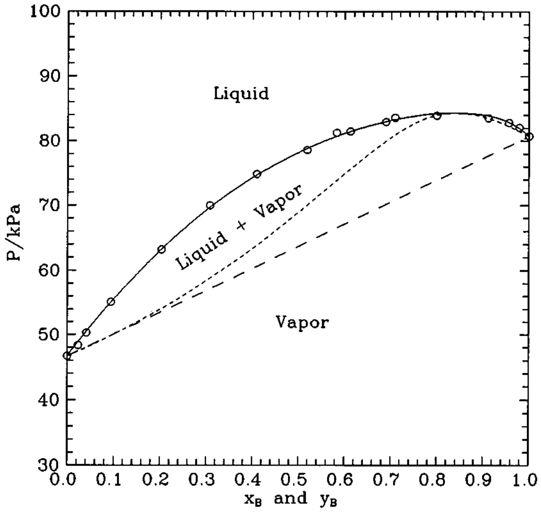

Figure 3. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (— —) for 2-(hexyloxy)ethanol (A) + 1,2-propanediol (B) at 180 °C.

measuring the pressure. The temperature of the material in the cell was measured with a platinum resistance thermometer inserted down a thermowell into the liquid in the cell. Temperatures were measured with an accuracy of ±0.05 K. The pressure was measured with a pressure transducer with an accuracy of ±0.5 kPa. The material in the cell was mixed with a magnetic stirrer.

The appropriate solvent was added to the evacuated cell to initiate a set of measurements. The bath temperature was then adjusted to give the desired cell temperature, and the solute was added until the pressure reached the desired level. Samples of the liquid phase were allowed to flash into a weighed receiver connected to a buret filled with water. Sample masses were measured with an accuracy of ±0.002 g. The gas flashing off the liquid in the receiver was collected in a 100 cm^3 buret for the dichloromethane system and in a 500 cm^3 buret for the propylene oxide systems. The volume of gas was measured to the nearest 0.1 cm^3. The temperature of the receiver, the temperature of the buret, and the barometric pressure were also measured at each point.

The receiver was kept at the temperature of dry ice to minimize the amount of solvent that passed through the receiver and into the buret. The gas also passed through a water bubbler prior to entering the buret to ensure that it was saturated with water. The water in the bubbler and buret was saturated with the solute prior to the measurements. Several samples were taken at each condition, and

Table 2. *PTx* Measurement Results on 2-(Hexyloxy)ethanol (A) + 1,2-Propanediol (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 = 100 °C[a]							
1	100.00	100.00	100.00	2.10	2.10	1.000	1.986	0.998	0.999	1.0000	1.0000	2.895
1	97.94	97.95	94.37	2.16	2.18	1.000	1.954	0.998	0.999	1.0000	1.0000	2.848
1	95.23	95.24	87.78	2.28	2.28	1.001	1.912	0.998	0.999	1.0000	1.0000	2.785
1	90.37	90.39	77.88	2.43	2.45	1.004	1.840	0.998	0.999	1.0000	1.0000	2.671
1	79.91	79.93	62.20	2.74	2.75	1.019	1.692	0.998	0.999	1.0000	1.0000	2.420
1	69.10	69.12	50.95	2.99	2.99	1.050	1.552	0.998	0.999	1.0000	1.0000	2.154
1	58.39	58.40	42.70	3.16	3.17	1.102	1.425	0.997	0.999	1.0001	1.0000	1.884
1	50.00	50.01	37.48	3.27	3.27	1.165	1.334	0.997	0.999	1.0001	1.0000	1.669
1	39.74	39.75	32.01	3.36	3.35	1.283	1.234	0.997	0.999	1.0001	1.0000	1.401
2	30.51	30.51	27.50	3.43	3.39	1.453	1.154	0.997	0.999	1.0001	1.0000	1.158
1	29.09	29.09	26.81	3.42	3.39	1.487	1.143	0.997	0.999	1.0001	1.0000	1.120
2	19.36	19.35	21.75	3.39	3.39	1.812	1.074	0.997	0.999	1.0001	1.0000	0.863
2	9.43	9.43	14.66	3.28	3.32	2.456	1.021	0.997	0.999	1.0001	1.0000	0.606
2	4.81	4.80	9.34	3.20	3.23	2.992	1.006	0.997	0.999	1.0001	1.0000	0.490
2	2.60	2.60	5.77	3.15	3.17	3.347	1.002	0.998	0.999	1.0001	1.0000	0.436
2	0.00	0.00	0.00	3.06	3.06	3.893	1.000	0.998	0.999	1.0001	1.0000	0.374
					t = 180 °C[b]							
1	100.00	100.00	100.00	46.68	46.68	1.000	1.753	0.979	0.993	1.0000	0.9992	3.000
1	97.57	97.66	93.39	48.35	48.88	1.000	1.728	0.978	0.992	1.0001	0.9993	2.956
1	95.70	95.85	88.78	50.30	50.53	1.001	1.709	0.977	0.992	1.0002	0.9993	2.921
1	90.30	90.58	77.34	55.09	55.06	1.003	1.654	0.975	0.991	1.0004	0.9994	2.819
1	79.25	79.68	60.17	63.19	63.26	1.015	1.544	0.972	0.988	1.0008	0.9996	2.596
1	68.77	69.20	48.67	69.97	69.71	1.039	1.444	0.969	0.987	1.0011	0.9998	2.369
1	58.69	59.05	40.29	74.85	74.72	1.078	1.352	0.967	0.985	1.0014	0.9999	2.137
1	47.89	48.14	33.15	78.60	78.86	1.146	1.260	0.966	0.984	1.0016	1.0000	1.872
2	41.60	41.74	29.54	81.27	80.74	1.205	1.210	0.965	0.984	1.0017	1.0000	1.709
1	38.62	38.77	27.95	81.47	81.48	1.239	1.188	0.965	0.984	1.0017	1.0000	1.632
2	30.97	31.06	24.02	82.95	83.02	1.353	1.133	0.965	0.983	1.0018	1.0001	1.426
1	29.02	29.08	23.02	83.60	83.33	1.390	1.120	0.965	0.983	1.0018	1.0001	1.371
2	20.02	20.05	18.30	83.92	84.26	1.622	1.066	0.965	0.983	1.0018	1.0001	1.119
2	8.89	8.85	10.84	83.56	83.92	2.168	1.016	0.965	0.983	1.0018	1.0001	0.799
2	4.43	4.39	6.41	82.83	82.88	2.553	1.004	0.966	0.983	1.0018	1.0000	0.671
2	2.15	2.13	3.46	82.07	81.97	2.816	1.001	0.967	0.983	1.0017	1.0000	0.607
2	0.00	0.00	0.00	80.74	80.74	3.122	1.000	0.968	0.983	1.0017	1.0000	0.547

[a] Wilson equation parameters: $\Lambda_{AB} = 0.2372$, $\Lambda_{BA} = 1.0794$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.2650$, $\Lambda_{BA} = 1.1897$.

Table 3. *PTx* Measurement Results on Acetone Cyanohydrin (A) + Acetone (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	0.037	0.037	1.000	0.463	1.000	1.000	1.0000	0.9993	301.375
1	97.50	97.50	11.23	0.58	0.32	1.000	0.473	1.000	1.000	1.0000	0.9993	308.306
1	95.21	95.22	5.95	0.74	0.60	0.999	0.483	0.999	1.000	1.0000	0.9993	314.970
1	89.57	89.59	2.52	1.25	1.32	0.995	0.509	0.999	0.999	1.0000	0.9993	332.959
1	82.61	82.64	1.31	2.00	2.33	0.984	0.543	0.998	0.999	1.0001	0.9993	358.678
1	73.38	73.41	0.68	3.57	3.86	0.961	0.592	0.997	0.999	1.0001	0.9994	400.421
2	65.32	65.33	0.42	5.41	5.42	0.929	0.638	0.995	0.998	1.0002	0.9994	446.481
1	63.75	63.79	0.38	5.55	5.75	0.921	0.648	0.995	0.998	1.0002	0.9994	456.519
2	55.00	55.02	0.23	7.90	7.74	0.871	0.703	0.993	0.997	1.0003	0.9995	523.342
1	53.88	53.91	0.22	8.14	8.01	0.864	0.710	0.993	0.997	1.0003	0.9995	533.190
2	44.67	44.70	0.13	10.82	10.45	0.793	0.771	0.991	0.996	1.0004	0.9996	630.443
1	43.28	43.30	0.12	11.39	10.84	0.780	0.781	0.990	0.996	1.0004	0.9996	648.144
2	32.08	32.12	0.06	14.96	14.26	0.669	0.857	0.987	0.995	1.0005	0.9997	828.959
2	21.81	21.86	0.03	18.35	17.69	0.547	0.922	0.984	0.993	1.0007	0.9998	1088.279
2	10.44	10.47	0.01	21.89	21.53	0.400	0.979	0.981	0.992	1.0008	0.9999	1574.946
2	5.08	5.09	0.00	23.37	23.21	0.331	0.995	0.979	0.991	1.0009	1.0000	1934.112
2	2.13	2.14	0.00	24.11	24.04	0.294	0.999	0.979	0.991	1.0009	1.0000	2186.869
2	0.00	0.00	0.00	24.60	24.60	0.268	1.000	0.978	0.991	1.0009	1.0000	2402.478
					t = 75 °C[b]							
1	100.00	100.00	100.00	1.64	1.64	1.000	0.514	0.999	1.000	1.0000	0.9950	54.578
1	96.02	96.06	29.90	5.96	5.26	0.999	0.539	0.997	0.999	1.0001	0.9951	57.230
1	92.16	92.25	16.57	9.37	9.11	0.996	0.564	0.995	0.998	1.0002	0.9952	59.940
1	84.44	84.60	7.70	17.76	17.86	0.985	0.614	0.990	0.996	1.0005	0.9955	65.833
1	74.81	75.04	3.90	30.08	30.78	0.961	0.678	0.983	0.993	1.0010	0.9958	74.152
1	64.42	64.66	2.12	46.12	47.27	0.922	0.746	0.974	0.989	1.0015	0.9963	84.555
1	54.52	54.75	1.24	64.40	65.28	0.874	0.808	0.964	0.985	1.0021	0.9968	96.082
2	52.28	52.33	1.09	70.7	70.0	0.860	0.822	0.962	0.984	1.0023	0.9969	99.169
1	43.55	43.74	0.70	87.72	87.53	0.809	0.870	0.952	0.979	1.0029	0.9974	111.064
2	40.78	40.87	0.60	95.6	93.6	0.790	0.885	0.949	0.978	1.0031	0.9976	115.390
1	32.35	32.46	0.37	113.80	112.05	0.732	0.925	0.939	0.974	1.0037	0.9981	129.279
2	31.27	31.39	0.35	116.7	114.4	0.725	0.930	0.938	0.973	1.0038	0.9981	131.177
2	21.37	21.49	0.18	140.1	136.6	0.652	0.966	0.926	0.968	1.0045	0.9987	150.431
2	9.92	10.00	0.06	164.5	161.8	0.564	0.992	0.912	0.962	1.0054	0.9994	177.115
2	5.04	5.09	0.03	174.0	172.0	0.526	0.998	0.907	0.960	1.0057	0.9997	190.257
2	2.10	2.12	0.01	178.5	178.0	0.503	1.000	0.904	0.958	1.0059	0.9999	198.750
2	0.00	0.00	0.00	182.1	182.1	0.487	1.000	0.902	0.957	1.0060	1.0000	205.102

[a] van Laar parameters: $C_{AB} = -1.3180$, $C_{BA} = -0.7708$. [b] van Laar parameters: $C_{AB} = -0.7191$, $C_{BA} = -0.6649$.

the measured results were averaged to give the reported solubility.

Due to the explosive hazard associated with pure oxygen, the oxygen and nitrogen solubility measurements were run at the same time. A mixture of approximately 1.76 mol % oxygen in nitrogen was prepared. This mixture was then used to bring the system to the desired pressure for each measurement. The technique described above was used to determine the total amount of oxygen and nitrogen dissolved in the liquid. Multiple GC analyses were then performed on liquid and vapor samples taken directly from the cell to determine the relative amounts of oxygen and nitrogen in each phase. The estimated uncertainty in the GC analyses was about ±2% of the measured ratio of oxygen to nitrogen.

The amount of solute dissolved in the liquid was measured with an accuracy of ±2% of the reported value. The vapor mole fraction of the solute was estimated from the Soave−Redlich−Kwong equation of state (Soave, 1972) so that apparent Henry's constants could be derived from the measured solubility data. The uncertainty in the estimated vapor compositions is mainly a function of the volatility of the solvent. At conditions where the vapor pressure of the solvent was quite small relative to the system pressure, the vapor phase was composed mainly of the solute. The predicted vapor composition of the solute at these conditions is estimated to be reliable to ±1%. The reliability of the predicted vapor composition decreases with an increase in solvent concentration in the vapor. At the conditions studied here, the highest solvent composition in the vapor was about 25 mol %. The prediction of the solute vapor concentration may have an uncertainty as great as ±3% at these conditions. Some of the measurements were performed at pressures greater than requested or at temperatures lower than requested in order to reduce the mole fraction of the solvent in the vapor phase to an acceptable level.

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 and activity and fugacity coefficients. The Wilson (Wilson, 1964) and van Laar (van Laar, 1910, 1913) activity coefficient models were used to represent the liquid-phase nonidealities. These equations are given below:

Wilson equation:

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

$$\ln \gamma_B = -\ln(x_B + \Lambda_{BA}x_A) - x_A\left(\frac{\Lambda_{AB}}{x_A + \Lambda_{AB}x_B} - \frac{\Lambda_{BA}}{\Lambda_{BA}x_A + x_B}\right) \tag{1}$$

van Laar equation:

$$\ln \gamma_A = C_{AB}\left(\frac{C_{BA}x_B}{C_{AB}x_A + C_{BA}x_B}\right)^2$$

$$\ln \gamma_B = C_{BA}\left(\frac{C_{AB}x_A}{C_{AB}x_A + C_{BA}x_B}\right)^2 \tag{2}$$

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. The procedure used to reduce the *PTx* data has been described earlier (Giles et al., 1996).

Solubility Data Reduction Procedure

Table 4. Vapor Pressure Measurements on Acetone Cyanohydrin

t/°C	P/kPa meas	P/kPa corr	% dev
44.77	0.255	0.259	−1.60
50.01	0.375	0.369	1.51
59.99	0.702	0.694	1.04
64.99	0.933	0.935	−0.23
69.99	1.239	1.244	−0.46
75.00	1.635	1.638	−0.20
80.00	2.129	2.131	−0.09

$\ln(P/\text{kPa}) = 14.0422 - 3416.36/(T/\text{K} - 96)$

The measured solubility data were converted to equilibrium liquid compositions by calculating the moles of gas collected from the liquid sample and the moles of solvent in the receiver. The volume of gas collected in the buret was equal to the volume of solute evolved from the liquid sample and the volume of the liquid sample. In addition, the gas in the buret contained a small amount of solvent, which vaporized as the sample flashed in the receiver, as well as water vapor from the water in the buret. Therefore, the net volume of solute was determined as follows

$$V_{gas} = V_{tot} - V_{solv} - V_{water} - \Delta V_{liq} \tag{3}$$

where V_{gas} is the volume of solute, V_{tot} is the total volume change observed in the buret, V_{solv} is the volume of the solvent vapor, V_{water} is the volume of the water vapor, and ΔV_{liq} is the volume of liquid sample collected in the receiver.

The mole fraction of solvent in the gas was equal to its vapor pressure at the temperature of the receiver divided by atmospheric pressure. The mole fraction of water in the gas was equal to its vapor pressure at the temperature of the buret divided by atmospheric pressure. The moles of solute gas were calculated by the ideal gas law as follows

$$n_{gas} = \frac{P_{atm}(V_{tot} - \Delta V_{liq})}{RT}(1 - y_{solv} - y_{water}) \tag{4}$$

where n_{gas} is the moles of solute, P_{atm} is the atmospheric pressure, R is the ideal gas constant, T is the temperature of the buret, y_{solv} is the vapor mole fraction of the solvent in the gas, and y_{water} is the vapor mole fraction of water in the gas.

The liquid in the receiver contained a small amount of dissolved solute at the flash conditions. The solute in the receiver was estimated from the apparent Henry's constant of the gas at the flash temperature and pressure as follows

$$x_{solute} = \frac{P_{atm}y_{solute}}{H_{flash}} \tag{5}$$

where x_{solute} is the liquid mole fraction of the solute dissolved in the solvent in the receiver, y_{solute} is the vapor mole fraction of solute in the receiver, and H_{flash} is the apparent Henry's constant of the solute at the flash temperature and pressure. An iterative procedure was used to obtain H_{flash} from the measured data.

The amount of solvent in a sample was calculated as the total weight of sample collected in the receiver less the amount of residual solute dissolved in the liquid. The amount of solvent that vaporized into the flash gas was included in the determination of the total amount of solvent.

The apparent Henry's constant is defined as Py_i/x_i, where P is the system pressure, y_i is the mole fraction of the solute in the vapor phase, and x_i is the mole fraction of the solute in the liquid phase. P and x_i were measured, while y_i was estimated by the Soave−Redlich−Kwong (Soave, 1972) equation of state.

The majority of the measurement conditions were adjusted to give nearly pure solute in the vapor phase,

Table 5. *PTx* Measurement Results on Acetone Cyanohydrin (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}
					$t = 15$ °C[a]							
1	100.00	100.00	100.00	0.024	0.024	1.000	1.064	1.000	1.000	1.0000	0.9987	2914.141
1	94.42	94.46	0.55	3.89	3.88	1.000	1.065	0.997	0.999	1.0001	0.9988	2909.580
1	90.04	90.12	0.30	7.00	6.91	1.000	1.065	0.994	0.998	1.0003	0.9989	2905.055
1	83.07	83.19	0.16	11.69	11.76	1.000	1.065	0.990	0.997	1.0004	0.9990	2895.778
1	73.59	73.73	0.09	18.24	18.37	1.001	1.063	0.985	0.995	1.0007	0.9991	2877.985
1	65.94	66.09	0.06	23.56	23.67	1.002	1.060	0.980	0.994	1.0009	0.9992	2857.990
1	56.49	56.62	0.04	30.03	30.18	1.005	1.055	0.975	0.992	1.0011	0.9993	2823.844
2	50.37	50.54	0.03	34.15	34.30	1.009	1.050	0.972	0.991	1.0013	0.9994	2794.765
1	46.18	46.28	0.03	37.17	37.16	1.012	1.046	0.969	0.990	1.0014	0.9994	2770.276
2	40.35	40.56	0.02	41.10	40.94	1.019	1.041	0.966	0.989	1.0016	0.9995	2730.833
2	29.72	29.94	0.02	48.14	47.80	1.041	1.029	0.961	0.987	1.0018	0.9996	2632.215
2	20.20	20.39	0.01	54.16	53.79	1.078	1.017	0.956	0.985	1.0020	0.9998	2504.881
2	10.62	10.75	0.00	60.08	59.76	1.146	1.006	0.951	0.984	1.0023	0.9999	2322.856
2	5.60	5.67	0.00	63.25	62.94	1.203	1.002	0.948	0.983	1.0024	0.9999	2198.394
2	2.68	2.72	0.00	65.22	64.84	1.247	1.001	0.947	0.982	1.0025	1.0000	2114.887
2	0.00	0.00	0.00	66.66	66.66	1.297	1.000	0.945	0.982	1.0025	1.0000	2029.803
					$t = 75$ °C[b]							
1	100.00	100.00	100.00	1.63	1.63	1.000	1.020	0.999	1.000	1.0000	0.9925	276.748
1	94.43	94.60	6.00	30.2[c]	26.1	1.000	1.020	0.987	0.996	1.0008	0.9929	274.466
1	90.07	90.34	3.32	46.2	45.6	1.000	1.020	0.978	0.993	1.0015	0.9932	272.608
1	83.11	83.50	1.84	76.7	77.0	1.000	1.020	0.963	0.988	1.0025	0.9937	269.528
1	73.64	74.11	1.07	120.2	120.7	1.000	1.019	0.942	0.981	1.0040	0.9944	265.075
1	66.00	66.47	0.75	156.0	156.6	1.001	1.018	0.925	0.976	1.0052	0.9949	261.243
1	56.54	56.97	0.51	201.8	201.7	1.002	1.016	0.904	0.969	1.0067	0.9956	256.159
2	50.43	51.01	0.41	231.0	230.2	1.003	1.014	0.891	0.964	1.0077	0.9961	252.762
1	46.22	46.55	0.35	252.3	251.6	1.005	1.013	0.882	0.961	1.0084	0.9964	250.103
2	40.43	41.17	0.28	278.6	277.6	1.007	1.011	0.870	0.957	1.0093	0.9968	246.746
2	29.80	30.61	0.18	329.2	329.0	1.014	1.008	0.847	0.949	1.0110	0.9976	239.588
2	20.27	21.00	0.11	375.4	376.2	1.023	1.004	0.826	0.942	1.0126	0.9983	232.289
2	10.67	11.16	0.06	425.5	425.3	1.039	1.002	0.804	0.934	1.0142	0.9991	223.806
2	5.63	5.92	0.03	452.8	452.0	1.051	1.000	0.793	0.930	1.0151	0.9995	218.765
2	2.70	2.84	0.01	469.5	467.9	1.059	1.000	0.786	0.927	1.0157	0.9998	215.616
2	0.00	0.00	0.00	482.8	482.8	1.068	1.000	0.780	0.925	1.0162	1.0000	212.558

[a] Wilson equation parameters: $\Lambda_{AB} = 0.3408$, $\Lambda_{BA} = 1.8166$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.5332$, $\Lambda_{BA} = 1.5634$. [c] Note: this point was not used in the *PTx* data reduction due to the inaccuracy in reading the pressure transducer at this low pressure.

Table 6. *PTx* Measurement Results on Propyl Mercaptan (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}
					$t = 70$ °C[a]							
1	100.00	100.00	100.00	110.0	110.0	1.000	1.740	0.969	0.982	1.0000	0.9726	10.928
1	99.23	99.36	93.47	117.3	117.2	1.000	1.728	0.967	0.981	1.0002	0.9729	10.845
1	96.68	97.20	76.64	141.9	140.9	1.000	1.688	0.961	0.977	1.0010	0.9738	10.569
1	92.11	93.21	57.65	183.6	182.4	1.003	1.620	0.950	0.969	1.0024	0.9754	10.080
1	84.80	86.55	40.84	244.8	245.7	1.010	1.518	0.933	0.958	1.0046	0.9779	9.318
1	76.77	78.87	30.47	309.6	310.9	1.025	1.416	0.916	0.947	1.0068	0.9804	8.517
1	64.36	66.43	21.18	402.0	403.0	1.063	1.283	0.892	0.931	1.0099	0.9840	7.366
1	56.02	57.80	17.06	459.4	459.7	1.102	1.209	0.877	0.921	1.0119	0.9862	6.659
1	46.27	47.56	13.32	522.5	522.1	1.163	1.139	0.861	0.910	1.0140	0.9886	5.905
1	36.50	37.26	10.21	579.8	582.0	1.244	1.084	0.845	0.900	1.0161	0.9910	5.224
2	30.48	31.89	8.73	617.7	612.9	1.295	1.062	0.837	0.895	1.0171	0.9922	4.897
1	28.51	28.88	7.92	628.9	630.3	1.326	1.050	0.833	0.892	1.0177	0.9929	4.721
2	23.76	25.00	6.89	656.9	652.9	1.371	1.038	0.827	0.888	1.0185	0.9938	4.502
2	10.71	11.46	3.29	739.5	734.6	1.563	1.008	0.806	0.874	1.0213	0.9970	3.802
2	5.66	6.11	1.80	773.0	769.2	1.658	1.002	0.798	0.868	1.0225	0.9984	3.549
2	2.56	2.78	0.83	793.9	791.4	1.724	1.000	0.792	0.864	1.0233	0.9992	3.398
2	0.00	0.00	0.00	810.5	810.5	1.784	1.000	0.787	0.861	1.0239	1.0000	3.276
					$t = 110$ °C[b]							
1	100.00	100.00	100.00	329.8	329.8	1.000	1.542	0.933	0.962	1.0000	0.9398	6.523
1	99.23	99.41	96.32	340.4	341.4	1.000	1.535	0.930	0.961	1.0004	0.9402	6.488
1	96.68	97.43	85.60	379.4	380.3	1.000	1.512	0.923	0.956	1.0016	0.9417	6.373
1	92.11	93.74	70.85	453.5	450.4	1.002	1.472	0.909	0.947	1.0039	0.9444	6.162
1	84.80	87.51	54.62	562.6	563.6	1.006	1.408	0.887	0.932	1.0075	0.9488	5.819
1	76.77	80.17	42.67	690.0	688.8	1.016	1.340	0.862	0.917	1.0116	0.9537	5.434
1	64.36	67.92	30.47	880.1	882.0	1.043	1.242	0.826	0.893	1.0179	0.9612	4.832
1	56.02	59.18	24.65	1006.9	1010.2	1.072	1.184	0.801	0.877	1.0221	0.9663	4.431
1	46.27	48.61	19.22	1155.6	1157.8	1.120	1.125	0.773	0.859	1.0269	0.9721	3.977
1	36.50	37.86	14.67	1297.7	1303.3	1.187	1.077	0.746	0.841	1.0317	0.9780	3.545
2	30.48	33.21	12.87	1374.1	1366.0	1.222	1.059	0.734	0.833	1.0338	0.9805	3.367
1	28.51	29.11	11.33	1418.0	1421.4	1.257	1.046	0.724	0.826	1.0357	0.9827	3.214
2	23.76	26.21	10.26	1468.7	1461.0	1.284	1.038	0.717	0.821	1.0370	0.9843	3.109
2	10.71	12.29	5.07	1666.7	1658.0	1.447	1.009	0.680	0.797	1.0435	0.9922	2.627
2	5.66	6.61	2.82	1750.1	1743.5	1.533	1.003	0.664	0.786	1.0464	0.9957	2.442
2	2.56	3.03	1.32	1804.4	1799.5	1.594	1.001	0.654	0.779	1.0483	0.9980	2.329
2	0.00	0.00	0.00	1848.3	1848.3	1.651	1.000	0.645	0.773	1.0499	1.0000	2.235

[a] Wilson equation parameters: $\Lambda_{AB} = 0.7036$, $\Lambda_{BA} = 0.7729$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.6650$, $\Lambda_{BA} = 0.9065$.

allowing its concentration to be reliably estimated from an equation of state. For the solubility measurements of oxygen and nitrogen in propylene oxide at 100 °C, the vapor solute concentration was as low as 75 mol %. Therefore, the estimation of the vapor concentration of the solute was less certain than that at conditions where the vapor was

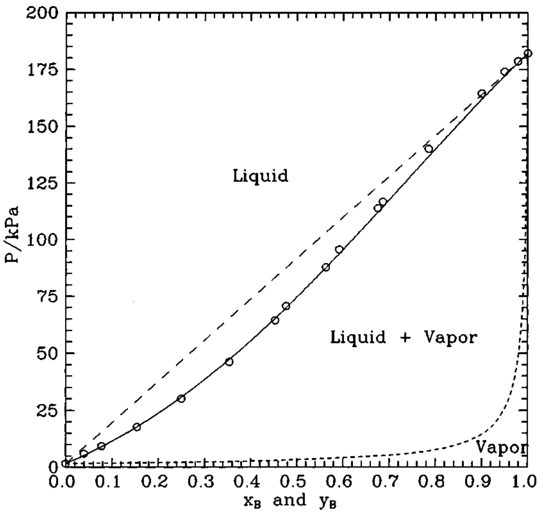

Figure 4. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (— —) for acetone cyanohydrin (A) + acetone (B) at 75 °C.

nearly pure solute. These estimations of the solute concentrations in the vapor phase should not be used as a basis for calculating the volatility of the solvent.

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 (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}). The relative volatility was determined from

$$\alpha_{BA} = \frac{y_B/x_B}{y_A/x_A} \qquad (6)$$

The activity coefficient parameters used to obtain the correlation are given at the bottom of each table. Figures showing total pressure as a function of liquid and vapor composition are included to illustrate the *PTx* data. Solubility measurement results are shown in tabular form, giving the system temperature and pressure, the derived composition of the solute in the vapor, the measured composition of the solute in the liquid, and the calculated apparent Henry's constant.

1. 2-(2-(Hexyloxy)ethoxy)ethanol + 1,2-Ethanediol. The results of the *PTx* measurements on 2-(2-(hexyloxy)-ethoxy)ethanol + 1,2-ethanediol at 100 and 180 °C are given in Table 1. The Wilson activity coefficient equation was used to reduce the data. The system pressure as a function of liquid and vapor composition at 180 °C is plotted in Figure 2 to illustrate the data. This system exhibits significant positive deviation from Raoult's law. The *PTx* data indicate the presence of minimum-boiling azeotropes at both temperatures in the dilute 2-(2-(hexyloxy)ethoxy)-ethanol region. It was not within the scope of this study to perform *PTxy* measurements to confirm the presence and composition of the apparent azeotrope. However, the carefully measured data show a definite increase in pressure upon adding small increments of 2-(2-(hexyloxy)-ethoxy)ethanol to 1,2-ethanediol at both temperatures. This measured increase in pressure and the fact that these data were measured in a glass still apparatus and that the system was well degassed throughout the *PTx* measurements strongly suggest the presence of an azeotrope.

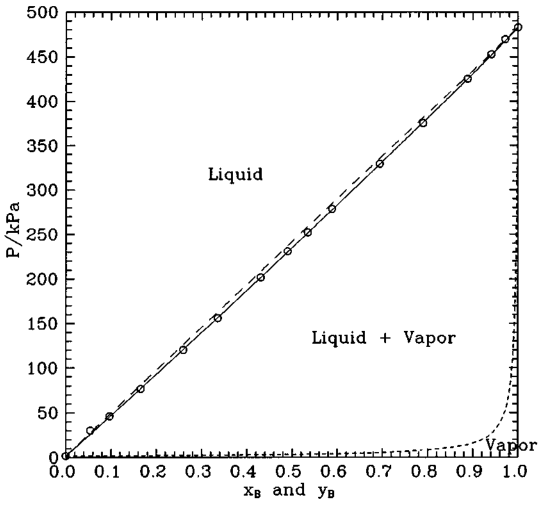

Figure 5. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (— —) for acetone cyanohydrin (A) + hydrogen cyanide (B) at 75 °C.

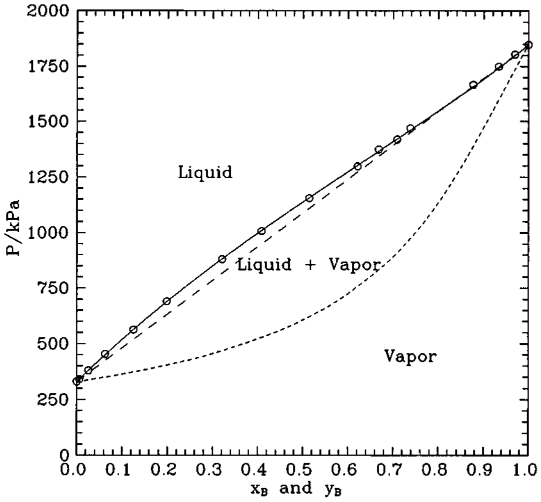

Figure 6. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (— —) for propyl mercaptan (A) + butane (B) at 110 °C.

Table 7. Solubility Measurement Results of Oxygen (A) and Nitrogen (B) in Propylene Oxide (C)

t/°C	P/MPa	$100y_A$[a]	$100x_A$[b]	(Py_A/x_A)/MPa	$100y_B$[a]	$100x_B$[b]	(Py_B/x_B)/MPa
25.0	3.447	1.620	0.0338	165.3	95.476	1.337	246.2
25.0	5.171	1.644	0.0495	171.8	96.049	1.984	250.4
25.0	6.895	1.665	0.0667	172.2	96.283	2.667	249.0
100.0	3.447	1.304	0.0363	123.9	73.273	1.590	158.8
100.0	5.171	1.403	0.0592	122.6	79.673	2.635	156.3
100.0	6.895	1.445	0.0800	124.5	82.787	3.592	158.9

[a] The concentration of propylene oxide in the vapor was determined using the Soave equation of state. The relative amount of oxygen and nitrogen in the vapor was determined by GC analysis. [b] Measured values.

2. 2-(Hexyloxy)ethanol + 1,2-Propanediol. Results of the *PTx* measurements on the 2-(hexyloxy)ethanol + 1,2-propanediol system at 100 and 180 °C are listed in Table 2, and the data at 180 °C are plotted in Figure 3. The Wilson activity coefficient equation was used to reduce the data. This system also shows significant positive deviation from ideality with minimum-boiling azeotropes at both temperatures.

3. Acetone Cyanohydrin + Acetone. The acetone cyanohydrin + acetone system exhibits negative deviation from Raoult's law at both 20 and 75 °C. Results of the *PTx* measurements are reported in Table 3, and the data at 75

Table 8. Solubility Measurement Results of Methane (A) in Dichloromethane (B)

t/°C	P/MPa	$100y_A$[a]	$100x_A$[b]	(Py_A/x_A)/MPa
−30.0	1.380	99.608	1.795	76.6
−30.0	2.759	99.723	3.613	76.2
−30.0	4.139	99.732	5.362	77.0
0.0	1.379	98.131	1.701	79.6
0.0	2.760	98.804	3.345	81.5
0.0	4.138	98.968	4.978	82.3
30.0	1.380	93.667	1.607	80.4
30.0	2.758	96.183	3.236	82.0
30.0	4.138	96.922	4.889	82.0

[a] Values calculated from the Soave equation of state. [b] Measured values.

Table 9. Constants Used in Data Reduction Procedure

compound	M_W	T_C/K	P_C/kPa	Z_C	ω	ref
2-(2-(hexyloxy)-ethoxy)ethanol	190.29	771.5	2026.5	0.240	0.80	*b*
1,2-ethanediol	62.068	645.0	7530	0.268	1.1367	*a*
2-(hexyloxy)ethanol	146.2	636.0	2738	0.2695	0.9235	*b*
1,2-propanediol	76.095	626.0	6100	0.280	1.1065	*a*
acetone cyanohydrin	85.106	647.0	4250	0.234	0.7334	*a*
acetone	58.080	508.2	4701.5	0.233	0.3064	*a*
hydrogen cyanide	27.026	456.65	5390.5	0.197	0.4102	*a*
propyl mercaptan	76.163	536.0	4630	0.264	0.2353	*a*
butane	58.123	425.18	3796.9	0.274	0.1993	*a*
propylene oxide	58.080	482.25	4924.4	0.228	0.2710	*a*
oxygen	31.999	154.58	5043.0	0.288	0.0218	*a*
nitrogen	28.014	126.10	3394.4	0.292	0.0403	*a*
dichloromethane	84.932	510.0	6079.5	0.265	0.1916	*a*
methane	16.043	190.56	4599.0	0.286	0.0115	*a*

[a] Measured and/or estimated values reported by Daubert et al. (1993). [b] Estimated using techniques shown in Chapter 2 of Reid et al. (1987).

Table 10. Measured and Literature Vapor Pressures

		P/kPa		
compound	t/°C	meas	lit.[a]	% dev[b]
2-(2-(hexyloxy)ethoxy)ethanol	100	0.249		
	180	9.805		
1,2-ethanediol	100	2.117	2.130	−0.63
	180	58.854	58.089	1.32
2-(hexyloxy)ethanol	100	2.099		
	180	46.679		
1,2-propanediol	100	3.061	3.034	0.88
	180	80.740	79.116	2.05
acetone cyanohydrin	15	0.024[c]	0.076	−68.42
	20	0.037[c]	0.107	−65.42
	75	1.635[c]	2.245	−27.17
acetone	20	24.600	24.585	0.06
	75	182.055	185.672	−1.95
hydrogen cyanide	15	66.656	66.913	−0.38
	75	482.804[d]	491.357	−1.74
propyl mercaptan	70	110.005	108.891	1.02
	110	329.84	328.303	0.47
butane	70	810.545	809.987	0.07
	110	1848.27	1848.18	0.005

[a] Literature data calculated from correlations in Daubert et al. (1993). [b] Percent deviation: 100 × (measured − literature)/literature. [c] The measured vapor pressure data for acetone cyanohydrin were obtained from an Antoine fit of vapor pressure data that were carefully measured in a still from 45 to 80 °C (see Table 4). Wiltec believes these vapor pressure data are accurate. [d] The vapor pressure of hydrogen cyanide at 75 °C was measured by Wiltec in conjunction with DIPPR project 805/92 (Giles et al., 1996) and found to be 482.36 kPa.

Table 11. Source and Purity of Chemicals

			purity, mass %	
compound	CAS no.[a]	supplier	Wiltec analysis	supplier analysis
2-(2-(hexyloxy)ethoxy)-ethanol	112-59-4	Aldrich	99.3	99.9
1,2-ethanediol	107-21-1	Aldrich	99.9+	99.99
2-(hexyloxy)ethanol	112-25-4	TCI America	98.4	99.1
1,2-propanediol	57-55-6	Aldrich	99.95+	99.9
acetone cyanohydrin	75-86-5	Aldrich		99.6
acetone	67-64-1	Aldrich	99.9+	99.9+
hydrogen cyanide	74-90-8	Fumico		99.6
propyl mercaptan	107-03-9	Aldrich		99.7
butane	106-97-8	Phillips		99.9+
propylene oxide	75-56-9	Aldrich		99.9
oxygen	7782-44-7	Air Products		99.999
nitrogen	7727-37-9	US Welding		99.99
dichloromethane	75-09-2	Aldrich		99.99
methane	74-82-8	US Welding		99.98

[a] Supplied by the authors.

°C are plotted in Figure 4. The measured *PTx* data were reduced using the van Laar activity coefficient equation.

The deviation between the measured and correlated pressure for each *PTx* point was much higher for this system than for any of the other systems studied. This is possibly due to decomposition of the acetone cyanohydrin during the course of the *PTx* runs. These measurements were performed as quickly and precisely as possible to minimize error in the total pressure measurements.

The vapor pressure of acetone cyanohydrin was measured in a glass still apparatus from about 45 to 80 °C. These results are reported in Table 4. Due to the low vapor pressure of the pure acetone cyanohydrin, adequate degassing of the pure component in conjunction with a *PTx* run was not possible. Therefore, the vapor pressure of pure acetone cyanohydrin that was used to reduce the *PTx* data was determined from the glass still measurements. The contents of the cell were thoroughly degassed after adding increments of acetone during the *PTx* runs.

4. Acetone Cyanohydrin + Hydrogen Cyanide. *PTx* data for the acetone cyanohydrin + hydrogen cyanide system were obtained at 15 and 75 °C. These data are reported in Table 5, and the data at 75 °C are plotted in Figure 5. The Wilson activity coefficient equation was used to reduce the data. This system shows nearly ideal behavior at both temperatures. The vapor pressure data of acetone cyanohydrin shown in Table 4 were used in reducing the *PTx* data.

5. Propyl Mercaptan + Butane. Results of the propyl mercaptan + butane system *PTx* measurements at 70 and 110 °C are reported in Table 6. The data were reduced using the Wilson activity coefficient equation. This system exhibits slight positive deviation from Raoult's law. The results of the 110 °C measurements are plotted in Figure 6.

6. Propylene Oxide + Oxygen. The results of the solubility measurements of oxygen in propylene oxide at 25 and 100 °C are shown in Table 7. These measurements were made at pressures of 3.447, 5.171, and 6.895 MPa at each of the two temperatures. The data show the apparent Henry's constant to be nearly independent of pressure at each of the two temperatures studied.

7. Propylene Oxide + Nitrogen. Solubility measurements of nitrogen in propylene oxide at 25 and 100 °C are also reported in Table 7. These measurements were made in conjunction with the oxygen measurements at pressures of 3.447, 5.171, and 6.895 MPa at each of the two temperatures. The nitrogen solubility data also show the apparent Henry's constant to be nearly independent of pressure at each of the two temperatures studied. The data also show nitrogen to be less soluble than oxygen in propylene oxide at the conditions that were studied.

8. Dichloromethane + Methane. Solubility measurements of methane in dichloromethane at −30, 0, and 30 °C are reported in Table 8. The solubility was measured at pressures of 1.380, 2.759, and 4.138 MPa at each of the three temperatures.

Ancillary Data. Table 9 gives the physical constants for each compound used in the data reduction procedure. Table 10 compares the measured pure component vapor pressures to correlations reported by Daubert et al. (1993). Table 11 lists the source and purity of the chemicals used in this study. The chemicals were degassed before being used whenever possible. Table 11 also lists the Chemical Abstracts Service Registry number for each chemical.

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