Phase Equilibria on Seven Binary Mixtures

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Vapor−liquid equilibria are reported for the following five systems: phenol + styrene; ethyl mercaptan + *n*-butane; *tert*-butyl mercaptan + propane; dimethyl ether + propane; trifluoroacetic acid + hydrogen chloride. The system pressure and temperature were measured at several charge compositions along two isotherms for each system. Equilibrium vapor- and liquid-phase compositions were derived from the *PTx* data using the Soave equation of state to represent the vapor phase and the Wilson or NRTL activity coefficient model to represent the liquid phase. Liquid−liquid equilibrium studies were performed on the dimethyl carbonate + water system at two temperatures by analyzing samples taken from each liquid phase. The solubility of hydrogen in α-methyl benzyl alcohol was measured at three pressures at each of 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 Projects 805/95 and 805/96 to obtain phase equilibrium data on seven binary systems. These systems and their measurement conditions are as follows:

1. Phenol + styrene at 60 and 100 °C.
2. Ethyl mercaptan + *n*-butane at 50 and 100 °C.
3. *tert*-Butyl mercaptan + propane at 10 and 60 °C.
4. Dimethyl ether + propane at 0 and 50 °C.
5. Trifluoroacetic acid and hydrogen chloride at −15 and +5 °C.
6. Dimethyl carbonate + water at 20 and 60 °C.
7. α-Methyl benzyl alcohol + hydrogen at 50, 100, and 150 °C.

Vapor−liquid equilibria were determined for the first five binary systems listed above 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. Liquid−liquid equilibrium data were obtained for the dimethyl carbonate + water binary system by directly analyzing each liquid phase. The solubility of hydrogen in α-methyl benzyl alcohol was determined by directly measuring the amount of hydrogen in the liquid at three pressures at each of three temperatures. 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 using the ITS-90 temperature scale with platinum resistance thermometers. These thermometers were calibrated using ice and steam points and referenced to a standard platinum resistance thermometer with a NIST traceable calibration. Temperatures were measured with a precision of ±0.01 K and an accuracy of ±0.05 K or better.

Measurements were performed in a glass still apparatus for system 1, the phenol + styrene binary system at 60 and 100 °C. Pressures measured using this apparatus are estimated to be accurate to within ±0.025 kPa.

The *PTx* measurements for systems 2−5 were performed using a stainless steel apparatus. When the run temperature was below 20 °C, system pressures of less than 100 kPa were measured using an external mercury manometer to within an estimated accuracy of ±0.05 kPa. Higher pressures were measured using a calibrated Paroscientific pressure transducer with an estimated accuracy of better than ±0.5 kPa.

The liquid−liquid equilibrium measurements for system 6 were performed in the glass cell apparatus shown in Figure 1. The cell was made of thick-walled borosilicate glass with a Teflon cap and had an internal volume of approximately 300 cm^3. The cap screwed into the cell and formed a seal with an O-ring. Small-bore lines through the cap were used for adding components, sampling, and pressure measurement. A thermowell into which a platinum resistance thermometer was inserted also extended into the cell. The cell pressure was measured with a Paroscientific pressure transducer.

Equal amounts of dimethyl carbonate and water were charged to the cell to initiate a run. The bath temperature was set at the desired value, and the cell and its contents were allowed to equilibrate at the appropriate temperature. The cell contents were stirred to help bring the system to equilibrium. Nitrogen was added to the cell to bring the system to about 40 kPa above ambient pressure. This was done to facilitate the withdrawal of the liquid samples.

The stirrer was then turned off, and the two liquid phases were allowed to separate. Samples from each phase were then withdrawn into weighed receivers and analyzed. The aqueous phase was analyzed for dimethyl carbonate using a gas chromatographic technique while the amount of water in the organic phase was determined by Karl Fischer titration. The reported compositions are estimated to be accurate to within ±1.5% of the analysis value.

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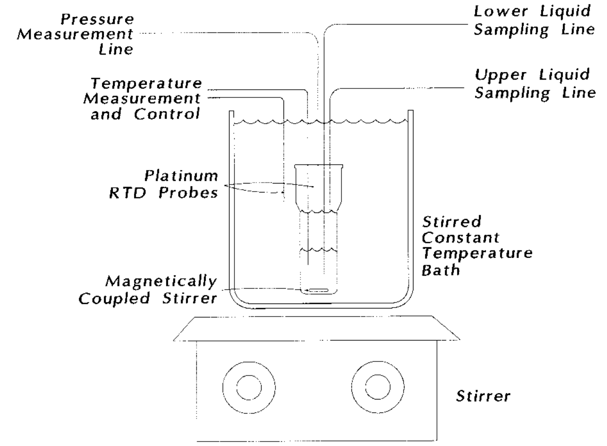

Figure 1. Glass liquid−liquid equilibrium apparatus.

The apparatus and procedures that were used to measure the solubility of hydrogen in α-methyl benzyl alcohol, system 7, have been previously described by Giles et al. (1997). The amount of hydrogen dissolved in the liquid was measured with an accuracy of ±0.5% of the reported value. The vapor mole fraction of hydrogen was estimated from the Soave−Redlich−Kwong equation of state (Soave, 1992) in order to derive apparent Henry's constants from the measured solubility data. The apparent Henry's constant (H) is defined as Py_{H_2}/x_{H_2}, where P is the system pressure, y_{H_2} is the mole fraction of hydrogen in the vapor phase, and x_{H_2} is the mole fraction of hydrogen in the liquid phase. The predicted vapor composition of hydrogen was well over 99 mol % at each of the conditions reported here and is estimated to be accurate to within ±0.25%. The reported apparent Henry's constants are estimated to be accurate to within ±1%.

Data Reduction Procedures

The results of the PTx measurements, which are the 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 NRTL (Renon and Prausnitz, 1968) activity coefficient models were used to represent the liquid-phase nonidealities. The activity coefficient model that gave the best overall fit of the measured total pressure data for a given system was generally used to reduce the data for that system. The 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 PTx data has been described earlier (Giles et al., 1996). An iterative procedure is used to solve the basic equation of vapor−liquid equilibrium, given as follows:

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

where P is the total pressure, y_i is the vapor mole fraction of component i, ϕ_i is the fugacity coefficient of component i, x_i is the liquid mole fraction of component i, γ_i is the activity coefficient of component i, P_i° is the vapor pressure of component i at system temperature, ϕ_i° is the fugacity coefficient of component i at system temperature and corresponding vapor pressure of component i, and the exponential term is the Poynting correction where V_i is the molar volume of component i. In the above expression it is assumed that the molar volume of component i is equal to the partial molar volume of component i at these conditions.

Table 1. PTx Measurement Results on Phenol (A) + Styrene (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}
						$t = 60\ °C$[a]						
1	100.00	100.00	100.00	0.66	0.66	1.000	2.531	1.000	1.000	1.0000	0.9998	19.66
1	96.43	96.44	59.24	1.08	1.08	1.001	2.400	0.999	0.999	1.0000	0.9998	18.63
1	91.50	91.53	38.48	1.58	1.58	1.006	2.235	0.999	0.999	1.0000	0.9998	17.27
1	80.78	80.81	22.43	2.45	2.45	1.030	1.931	0.999	0.999	1.0001	0.9999	14.57
1	70.91	70.94	16.49	3.05	3.04	1.071	1.705	0.998	0.998	1.0001	0.9999	12.36
1	70.56	70.59	16.34	3.06	3.06	1.073	1.698	0.998	0.998	1.0001	0.9999	12.29
1	60.29	60.32	12.91	3.52	3.53	1.143	1.508	0.998	0.998	1.0001	0.9999	10.25
1	51.26	51.28	10.86	3.83	3.85	1.232	1.371	0.998	0.998	1.0001	0.9999	8.643
2	50.61	50.63	10.73	3.87	3.87	1.240	1.362	0.998	0.998	1.0001	0.9999	8.533
1	44.81	44.82	9.67	4.03	4.04	1.319	1.288	0.998	0.998	1.0001	1.0000	7.588
2	39.56	39.58	8.80	4.18	4.18	1.407	1.228	0.998	0.998	1.0001	1.0000	6.786
2	31.03	31.04	7.47	4.40	4.39	1.597	1.147	0.998	0.997	1.0001	1.0000	5.579
2	19.96	19.98	5.63	4.65	4.64	1.980	1.066	0.998	0.997	1.0001	1.0000	4.181
2	9.86	9.87	3.45	4.88	4.88	2.581	1.018	0.997	0.997	1.0001	1.0000	3.064
2	5.15	5.15	2.05	5.00	5.00	3.013	1.005	0.997	0.997	1.0001	1.0000	2.592
2	0.00	0.00	0.00	5.14	5.14	3.675	1.000	0.997	0.997	1.0001	1.0000	2.115
						$t = 100\ °C$[b]						
1	100.00	100.00	100.00	5.48	5.48	1.000	2.243	0.998	0.998	1.0000	0.9992	10.33
1	94.21	94.27	63.31	8.17	8.19	1.002	2.073	0.997	0.996	1.0001	0.9993	9.529
1	88.10	88.19	46.10	10.62	10.62	1.010	1.915	0.996	0.995	1.0002	0.9994	8.736
1	80.52	80.64	34.74	13.09	13.12	1.028	1.745	0.995	0.994	1.0002	0.9995	7.824
1	71.05	71.17	26.68	15.66	15.62	1.063	1.566	0.994	0.993	1.0003	0.9996	6.787
1	60.00	60.09	20.88	17.96	17.90	1.129	1.397	0.993	0.992	1.0004	0.9997	5.705
1	51.40	51.47	17.65	19.42	19.33	1.202	1.291	0.993	0.992	1.0004	0.9998	4.950
1	45.06	45.12	15.63	20.27	20.26	1.272	1.225	0.992	0.991	1.0004	0.9998	4.438
2	40.96	41.03	14.43	20.66	20.80	1.326	1.187	0.992	0.991	1.0005	0.9998	4.127
2	30.88	30.95	11.60	21.93	22.04	1.497	1.109	0.992	0.991	1.0005	0.9999	3.416
2	19.94	19.99	8.39	23.29	23.30	1.769	1.048	0.991	0.990	1.0005	0.9999	2.730
2	10.87	10.90	5.22	24.31	24.31	2.107	1.015	0.991	0.990	1.0006	1.0000	2.221
2	4.90	4.91	2.62	24.99	24.96	2.415	1.003	0.991	0.989	1.0006	1.0000	1.916
2	0.00	0.00	0.00	25.49	25.49	2.742	1.000	0.990	0.989	1.0006	1.0000	1.682

[a] Wilson equation parameters: $\Lambda_{AB} = 0.3460$; $\Lambda_{BA} = 0.7598$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.4621$; $\Lambda_{BA} = 0.7633$.

Table 2. *PTx* Measurement Results on Ethyl Mercaptan (A) + *n*-Butane (B)

				P/kPa								
run no.	$100z_A$	$100x_A$	$100y_A$	meas	calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
				$t = 50$ °C[a]								
1	100.00	100.00	100.00	167.6	167.6	1.000	2.028	0.963	0.966	1.0000	0.9870	5.513
1	97.23	97.44	87.82	186.6	187.0	1.001	1.946	0.959	0.962	1.0006	0.9877	5.286
1	95.37	95.70	81.26	200.2	199.3	1.002	1.893	0.956	0.959	1.0009	0.9882	5.139
1	90.71	91.28	68.60	227.7	227.9	1.006	1.773	0.950	0.953	1.0017	0.9893	4.789
1	81.54	82.32	52.73	275.3	275.7	1.024	1.574	0.939	0.943	1.0031	0.9912	4.175
1	73.06	73.86	43.37	312.1	312.0	1.052	1.429	0.931	0.936	1.0042	0.9927	3.689
1	63.76	64.44	35.92	345.3	345.3	1.096	1.305	0.924	0.929	1.0051	0.9940	3.232
1	53.44	53.92	29.44	376.9	376.7	1.161	1.200	0.917	0.923	1.0060	0.9952	2.805
2	46.58	46.92	25.67	395.0	395.4	1.215	1.146	0.913	0.919	1.0066	0.9960	2.561
1	44.06	44.35	24.34	401.7	401.9	1.237	1.129	0.911	0.918	1.0068	0.9962	2.477
2	39.51	39.73	22.01	413.3	413.2	1.280	1.101	0.909	0.915	1.0071	0.9967	2.336
2	28.48	28.82	16.56	438.7	438.3	1.399	1.051	0.903	0.910	1.0078	0.9977	2.039
2	17.65	17.89	10.88	462.2	461.7	1.548	1.019	0.898	0.905	1.0085	0.9986	1.786
2	9.03	9.15	5.90	479.5	479.3	1.694	1.005	0.894	0.902	1.0090	0.9993	1.609
2	4.46	4.52	3.02	487.5	488.1	1.783	1.001	0.892	0.900	1.0093	0.9997	1.523
2	0.00	0.00	0.00	496.3	496.3	1.878	1.000	0.890	0.898	1.0095	1.0000	1.444
				$t = 100$ °C[b]								
1	100.00	100.00	100.00	639.9	639.9	1.000	1.739	0.905	0.915	1.0000	0.9650	3.485
1	97.23	97.62	92.39	680.6	681.7	1.000	1.683	0.899	0.909	1.0011	0.9666	3.371
1	95.37	95.99	87.88	709.9	708.9	1.001	1.648	0.895	0.905	1.0019	0.9677	3.297
1	90.71	91.78	78.18	774.4	774.4	1.004	1.564	0.885	0.897	1.0037	0.9702	3.118
1	81.54	83.09	63.76	891.3	891.6	1.018	1.421	0.868	0.881	1.0069	0.9748	2.793
1	73.06	74.69	53.85	987.7	987.6	1.040	1.315	0.854	0.868	1.0095	0.9786	2.528
1	63.76	65.17	45.14	1081.1	1081.6	1.073	1.222	0.840	0.856	1.0121	0.9823	2.275
1	53.44	54.43	37.00	1174.3	1174.4	1.122	1.143	0.826	0.844	1.0147	0.9860	2.034
2	46.58	47.27	32.11	1229.9	1230.7	1.161	1.103	0.817	0.836	1.0162	0.9882	1.896
1	44.06	44.64	30.37	1250.2	1250.5	1.177	1.091	0.815	0.833	1.0168	0.9890	1.848
2	39.51	39.91	27.31	1284.5	1284.9	1.207	1.071	0.809	0.829	1.0177	0.9904	1.768
2	28.48	29.20	20.43	1358.2	1358.3	1.285	1.036	0.798	0.819	1.0198	0.9933	1.606
2	17.65	18.17	13.18	1428.4	1427.6	1.379	1.013	0.788	0.810	1.0217	0.9961	1.462
2	9.03	9.31	7.01	1479.2	1478.2	1.466	1.003	0.780	0.803	1.0231	0.9981	1.361
2	4.46	4.60	3.54	1502.6	1503.0	1.517	1.001	0.776	0.800	1.0238	0.9991	1.312
2	0.00	0.00	0.00	1525.5	1525.5	1.569	1.000	0.773	0.797	1.0244	1.0000	1.266

[a] Wilson equation parameters: $\Lambda_{AB} = 0.7857$; $\Lambda_{BA} = 0.6110$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.9410$; $\Lambda_{BA} = 0.6101$.

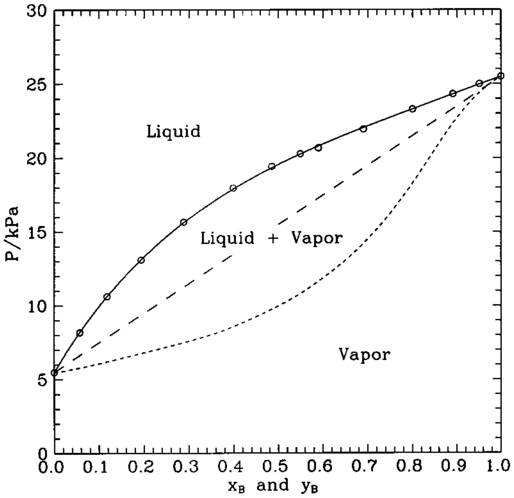

Figure 2. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (— —) for phenol (A) + styrene (B) at 100 °C.

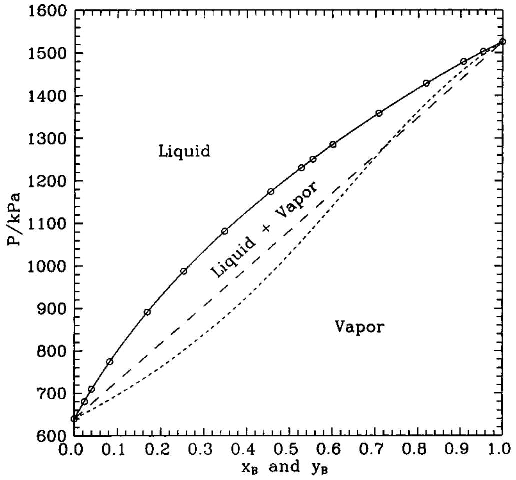

Figure 3. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (— —) for ethyl mercaptan (A) + *n*-butane (B) at 100 °C.

There is an added complexity when working with trifluoroacetic acid (TFA) because it associates in the vapor phase. This association can be represented by assuming that TFA exists as monomer and dimer molecules in equilibrium. The equilibrium is expressed by the following equation from Gmehling et al. (1982):

$$\log K_p = -9.925 + \frac{3053}{T/K} \tag{2}$$

The equilibrium constant in eq 2 has units of kPa^{-1}.

The partial pressure of the monomer is equal to its vapor mole fraction multiplied by the total pressure, and the partial pressure of the dimer is found from the following equation:

$$K_p = \frac{P_{\text{dimer}}}{{P_{\text{monomer}}}^2} \tag{3}$$

The data reduction now involves solving eq 1 for the TFA monomer and HCl. The vapor pressure of the TFA monomer is taken as its partial pressure over pure liquid TFA at the temperature of interest.

The measured solubility data for the α-methyl benzyl alcohol + hydrogen binary system were converted to

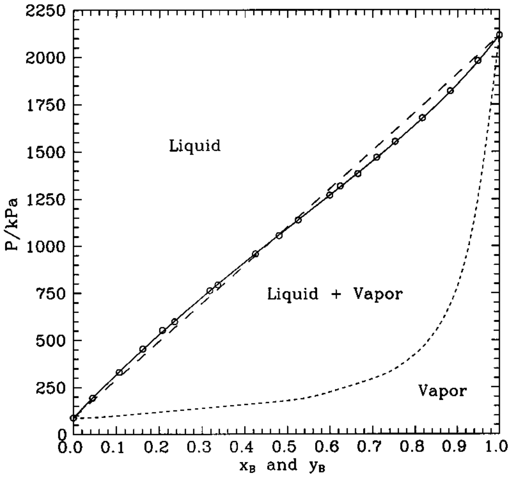

Figure 4. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (— —) for *tert*-butyl mercaptan (A) + propane (B) at 60 °C.

equilibrium liquid compositions using procedures similar to those described previously by Giles et al. (1997). The system pressure and the liquid composition were measured while the vapor composition was estimated by the Soave−Redlich−Kwong (Soave, 1972) equation of state. Well over 99 mol % hydrogen was present in the vapor phase at the conditions reported here, allowing its concentration to be reliably estimated from an equation of state. However, it should be noted that these estimates of the hydrogen concentration in the vapor phase should not be used as a basis for calculating the volatility of α-methyl benzyl alcohol.

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) on a molar basis, the calculated liquid (x_A) and vapor (y_A) compositions on a molar basis, 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

$$\alpha_{BA} = \frac{y_B/x_B}{y_A/x_A} \tag{4}$$

The activity coefficient parameters used in the correlation

Table 3. *PTx* Measurement Results on *tert*-Butyl Mercaptan (A) + Propane (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 = 10 °C[a]							
1	100.00	100.00	100.00	12.32	12.32	1.000	1.653	0.994	0.999	1.0000	0.9775	74.12
3	94.28	94.91	20.99	57.03	57.00	1.001	1.586	0.974	0.990	1.0021	0.9791	70.25
3	86.80	88.01	10.11	112.51	113.29	1.006	1.503	0.951	0.980	1.0048	0.9811	65.27
3	80.67	82.16	6.99	158.6	157.4	1.014	1.438	0.933	0.972	1.0069	0.9827	61.27
1	74.99	76.96	5.46	195.4	194.2	1.024	1.385	0.918	0.966	1.0086	0.9840	57.86
3	72.78	74.43	4.92	211.0	211.3	1.030	1.361	0.911	0.963	1.0095	0.9847	56.26
1	63.70	65.64	3.62	266.5	267.3	1.056	1.283	0.889	0.953	1.0121	0.9867	50.92
3	62.70	64.25	3.46	275.1	275.7	1.061	1.271	0.886	0.951	1.0125	0.9870	50.11
1	53.58	55.19	2.66	327.2	328.1	1.102	1.203	0.865	0.942	1.0150	0.9889	45.02
3	49.22	50.34	2.33	354.0	354.7	1.129	1.170	0.854	0.937	1.0163	0.9898	42.42
1	44.49	45.68	2.06	379.3	379.5	1.160	1.142	0.845	0.933	1.0175	0.9907	40.01
3	38.43	39.10	1.72	413.4	413.9	1.211	1.106	0.831	0.927	1.0192	0.9920	36.73
1	35.73	36.49	1.59	427.6	427.4	1.235	1.093	0.826	0.925	1.0198	0.9924	35.46
3	28.53	28.82	1.25	467.3	466.9	1.317	1.059	0.811	0.918	1.0217	0.9939	31.87
2	22.92	26.15	1.14	482.7	480.8	1.350	1.049	0.805	0.915	1.0224	0.9944	30.67
1	24.26	24.51	1.07	490.0	489.4	1.372	1.044	0.802	0.914	1.0228	0.9947	29.95
2	14.23	15.46	0.70	541.0	538.7	1.516	1.018	0.783	0.905	1.0252	0.9965	26.05
2	9.96	10.51	0.49	569.5	567.5	1.615	1.009	0.772	0.900	1.0266	0.9975	24.01
2	4.97	5.05	0.24	603.6	601.4	1.745	1.002	0.760	0.894	1.0282	0.9988	21.85
4	0.00	0.00	0.00	635.6	635.6	1.891	1.000	0.747	0.888	1.0299	1.0000	19.91
					t = 60 °C[b]							
1	100.00	100.00	100.00	88.27	88.27	1.000	1.582	0.971	0.995	1.0000	0.9270	27.18
3	94.28	95.53	45.31	193.3	193.2	1.001	1.530	0.941	0.981	1.0045	0.9307	25.80
3	86.80	89.30	25.82	330.1	333.2	1.004	1.463	0.903	0.965	1.0106	0.9355	23.97
3	80.67	83.87	18.79	453.2	449.8	1.010	1.409	0.873	0.952	1.0157	0.9396	22.47
1	74.99	79.30	15.27	551.9	544.3	1.017	1.366	0.849	0.941	1.0198	0.9430	21.26
3	72.78	76.46	13.66	597.9	601.6	1.023	1.341	0.834	0.935	1.0224	0.9450	20.53
1	63.70	68.24	10.39	762.6	761.3	1.043	1.273	0.795	0.917	1.0294	0.9506	18.54
3	62.70	66.35	9.82	793.6	796.9	1.049	1.259	0.786	0.913	1.0310	0.9519	18.10
1	53.58	57.54	7.74	957.2	958.7	1.082	1.197	0.747	0.896	1.0382	0.9577	16.15
3	49.22	51.96	6.73	1054.6	1058.5	1.109	1.162	0.723	0.885	1.0427	0.9613	14.99
1	44.49	47.50	6.03	1137.4	1137.6	1.134	1.137	0.704	0.876	1.0462	0.9641	14.10
3	38.43	40.04	5.00	1269.0	1269.2	1.184	1.099	0.674	0.862	1.0522	0.9689	12.68
1	35.73	37.62	4.70	1317.7	1312.2	1.203	1.088	0.664	0.857	1.0541	0.9704	12.24
2	22.92	33.48	4.19	1382.7	1386.5	1.239	1.071	0.647	0.849	1.0575	0.9731	11.50
3	28.53	29.10	3.68	1468.9	1466.7	1.282	1.054	0.628	0.841	1.0612	0.9760	10.74
1	24.26	24.77	3.18	1552.6	1548.4	1.330	1.040	0.610	0.832	1.0649	0.9790	10.00
2	14.23	18.34	2.44	1677.5	1675.7	1.414	1.022	0.582	0.818	1.0708	0.9837	8.966
2	9.96	11.73	1.65	1820.7	1818.0	1.521	1.009	0.550	0.802	1.0774	0.9889	7.934
2	4.97	5.16	0.78	1979.7	1975.6	1.650	1.002	0.516	0.785	1.0847	0.9948	6.946
4	0.00	0.00	0.00	2115.4	2115.4	1.774	1.000	0.486	0.770	1.0912	1.0000	6.189

[a] Wilson equation parameters: $\Lambda_{AB} = 0.5642$; $\Lambda_{BA} = 0.9355$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.5928$; $\Lambda_{BA} = 0.9497$.

Table 4. *PTx* Measurement Results on Dimethyl Ether (A) + Propane (B)

run no.	$100z_A$	$100x_A$	$100y_A$	P/kPa meas	P/kPa calc	γ_A	γ_B	ϕ_A	ϕ_B	PF_A	PF_B	α_{BA}
					$t = 0$ °C[a]							
1	100.00	100.00	100.00	266.3	266.3	1.000	1.792	0.948	0.948	1.0000	0.9924	3.032
1	98.07	98.14	94.69	276.8	276.8	1.000	1.752	0.946	0.946	1.0003	0.9928	2.964
1	94.45	94.62	86.11	295.6	295.2	1.002	1.681	0.942	0.942	1.0008	0.9934	2.840
1	89.88	90.15	77.27	316.5	316.2	1.006	1.600	0.938	0.938	1.0015	0.9942	2.692
1	80.33	80.68	63.44	353.2	353.5	1.022	1.453	0.931	0.931	1.0025	0.9956	2.406
1	70.76	71.08	53.32	383.3	383.5	1.050	1.335	0.925	0.925	1.0034	0.9967	2.151
1	60.50	60.73	44.75	408.7	409.2	1.094	1.234	0.920	0.920	1.0042	0.9976	1.909
2	56.01	56.15	41.41	419.0	418.8	1.118	1.197	0.918	0.918	1.0045	0.9980	1.812
1	52.54	52.69	39.00	425.5	425.5	1.139	1.171	0.916	0.917	1.0047	0.9982	1.742
2	49.68	49.84	37.08	430.9	430.7	1.157	1.152	0.915	0.916	1.0048	0.9984	1.686
1	47.35	47.46	35.50	434.9	434.8	1.173	1.137	0.915	0.915	1.0049	0.9986	1.641
2	42.38	42.54	32.30	442.6	442.6	1.210	1.109	0.913	0.914	1.0052	0.9988	1.552
2	35.46	35.62	27.83	452.1	452.2	1.269	1.075	0.911	0.912	1.0054	0.9992	1.435
2	21.75	21.84	18.55	466.9	466.8	1.419	1.028	0.908	0.909	1.0059	0.9997	1.227
2	13.21	13.25	12.07	472.9	472.4	1.538	1.010	0.907	0.908	1.0060	0.9999	1.112
2	4.47	4.47	4.45	475.4	474.7	1.687	1.001	0.907	0.908	1.0061	1.0000	1.005
2	2.43	2.43	2.47	474.6	474.6	1.726	1.000	0.907	0.908	1.0061	1.0000	0.982
2	0.00	0.00	0.00	474.2	474.2	1.774	1.000	0.907	0.908	1.0061	1.0000	0.955
					$t = 50$ °C[b]							
1	100.00	100.00	100.00	1140.6	1140.6	1.000	1.493	0.862	0.864	1.0000	0.9794	2.019
1	98.07	98.21	96.50	1165.6	1165.9	1.000	1.469	0.859	0.861	1.0007	0.9803	1.985
1	94.45	94.79	90.44	1211.8	1211.4	1.001	1.424	0.853	0.855	1.0020	0.9819	1.923
1	89.88	90.41	83.60	1264.2	1265.2	1.004	1.373	0.847	0.849	1.0035	0.9839	1.849
1	80.33	81.02	71.47	1365.0	1365.2	1.016	1.279	0.834	0.837	1.0063	0.9875	1.704
1	70.76	71.38	61.33	1449.8	1450.3	1.036	1.203	0.824	0.827	1.0087	0.9906	1.573
1	60.50	60.93	51.84	1526.7	1526.5	1.065	1.139	0.815	0.818	1.0109	0.9933	1.449
2	56.01	56.25	47.90	1556.8	1555.9	1.081	1.116	0.811	0.814	1.0117	0.9944	1.398
1	52.54	52.80	45.08	1575.5	1575.9	1.093	1.100	0.809	0.812	1.0123	0.9952	1.363
2	49.68	49.97	42.79	1591.2	1591.3	1.105	1.089	0.807	0.810	1.0127	0.9957	1.335
1	47.35	47.52	40.84	1603.8	1603.8	1.115	1.079	0.805	0.808	1.0131	0.9962	1.312
2	42.38	42.68	37.01	1626.1	1626.7	1.136	1.063	0.802	0.806	1.0137	0.9970	1.267
2	35.46	35.75	31.54	1654.1	1654.9	1.170	1.043	0.799	0.802	1.0145	0.9980	1.208
2	21.75	21.90	20.30	1694.5	1695.0	1.249	1.015	0.794	0.798	1.0157	0.9995	1.101
2	13.21	13.27	12.79	1708.1	1708.2	1.307	1.005	0.792	0.796	1.0160	1.0000	1.043
2	4.47	4.46	4.51	1710.4	1711.2	1.373	1.001	0.792	0.796	1.0161	1.0001	0.988
2	2.43	2.42	2.48	1709.8	1710.2	1.389	1.000	0.792	0.796	1.0161	1.0001	0.976
2	0.00	0.00	0.00	1708.2	1708.2	1.409	1.000	0.792	0.796	1.0160	1.0000	0.962

[a] Wilson equation parameters: $\Lambda_{12} = 0.7462$; $\Lambda_{21} = 0.7193$. [b] Wilson equation parameters: $\Lambda_{12} = 0.9625$; $\Lambda_{21} = 0.6952$.

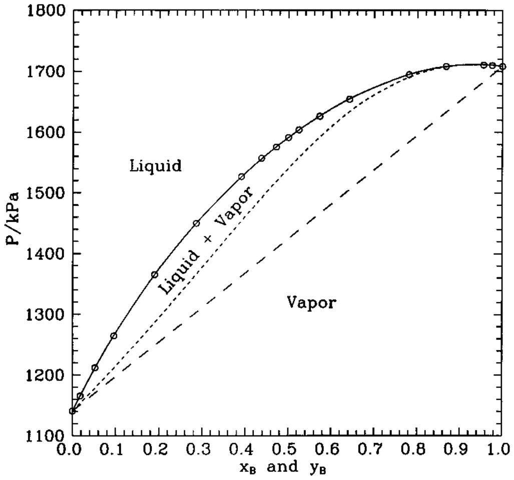

Figure 5. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (− −) for dimethyl ether (A) + propane (B) at 50 °C.

are given at the bottom of each table. Figures showing the total pressure as a function of liquid and vapor compositions are included to illustrate the *PTx* data.

Liquid−liquid equilibrium measurement results are shown in tabular form, giving the results of the sample analyses of each liquid phase on a molar basis at each temperature. This table also includes the standard deviations obtained from the analyses of multiple samples that were withdrawn from each liquid phase.

Solubility measurement results are shown in tabular form, giving the system temperature and pressure, the derived composition of hydrogen in the vapor, the measured composition of hydrogen in the liquid, and the calculated apparent Henry's constant (*H*).

1. Phenol + Styrene. Results of the *PTx* measurements on phenol + styrene at 60 and 100 °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 100 °C is plotted in Figure 2 to illustrate the data. This system exhibits moderate positive deviation from Raoult's law. The expression $P = \sum(P_i^\circ x_i)$ defines Raoult's law, where P is the total system pressure, P_i° is the vapor pressure of component i, and x_i is the liquid mole fraction of component i. The styrene contained 0.1 mass % 4-*tert*-butylcatechol as an inhibitor.

2. Ethyl Mercaptan + *n*-Butane. The results of the *PTx* measurements on ethyl mercaptan + *n*-butane at 50 and 100 °C are given in Table 2. The Wilson activity coefficient equation was used to reduce the data. These data are plotted in Figure 3 for the 100 °C measurements. This system exhibits positive deviation from Raoult's law.

3. *tert*-Butyl Mercaptan + Propane. Results of measurements on *tert*-butyl mercaptan + propane at 10 and 60 °C are reported in Table 3. The data were reduced using the Wilson activity coefficient equation. The results of the

Table 5. *PTx* Measurement Results on Trifluoroacetic Acid (A) + Hydrogen Chloride (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}
					$t = -15$ °C[a]							
1	100.00	100.00	100.00	1.40	1.40	1.000	3.166	1.000	1.000	1.0000	0.9704	2323.8
3	94.21	96.21	1.22	164.2	163.0	1.002	2.912	0.957	0.987	1.0055	0.9732	2052.9
3	91.21	94.06	0.82	244.6	245.3	1.004	2.786	0.937	0.980	1.0083	0.9746	1922.3
3	82.55	87.23	0.43	469.5	473.2	1.017	2.450	0.880	0.962	1.0161	0.9785	1584.2
1	81.30	85.96	0.40	509.4	511.1	1.021	2.396	0.871	0.959	1.0174	0.9791	1531.5
3	72.12	77.75	0.28	725.1	725.9	1.051	2.103	0.820	0.942	1.0249	0.9828	1249.9
1	70.71	76.09	0.26	768.4	764.3	1.058	2.053	0.811	0.939	1.0262	0.9834	1202.8
3	60.99	66.35	0.20	969.7	965.1	1.115	1.805	0.764	0.923	1.0332	0.9869	970.3
1	58.93	63.85	0.19	1015.4	1010.6	1.133	1.751	0.754	0.919	1.0348	0.9877	920.4
1	49.90	53.87	0.16	1174.7	1172.9	1.225	1.566	0.718	0.906	1.0405	0.9905	748.7
3	47.42	51.31	0.15	1209.8	1210.0	1.255	1.525	0.710	0.903	1.0418	0.9911	710.1
1	40.97	43.78	0.13	1305.6	1308.9	1.365	1.414	0.688	0.895	1.0453	0.9928	604.7
3	38.35	40.97	0.12	1336.6	1341.9	1.416	1.376	0.681	0.892	1.0465	0.9934	568.0
2	24.74	33.37	0.11	1414.2	1421.3	1.600	1.280	0.664	0.886	1.0493	0.9948	472.2
1	29.68	31.05	0.10	1437.7	1442.7	1.675	1.253	0.659	0.884	1.0501	0.9952	443.7
3	25.57	26.58	0.09	1475.5	1480.1	1.855	1.202	0.651	0.881	1.0514	0.9958	389.0
2	15.93	19.21	0.08	1538.6	1533.3	2.321	1.125	0.640	0.877	1.0533	0.9967	299.1
2	9.80	10.85	0.06	1608.1	1589.8	3.445	1.051	0.628	0.873	1.0553	0.9977	199.8
2	5.32	5.54	0.04	1660.7	1636.6	5.068	1.016	0.619	0.869	1.0570	0.9985	145.4
4	0.00	0.00	0.00	1720.3	1720.3	9.231	1.000	0.601	0.862	1.0600	1.0000	126.1
					$t = 5$ °C[b]							
1	100.00	100.00	100.00	5.08	5.08	1.000	2.940	0.999	1.001	1.0000	0.9492	1020.0
3	94.21	96.64	3.08	219.6	217.8	1.001	2.735	0.953	0.986	1.0069	0.9528	906.5
3	91.21	94.74	2.07	328.7	329.0	1.003	2.632	0.930	0.979	1.0105	0.9547	850.9
3	82.55	88.57	1.09	643.8	649.9	1.013	2.348	0.866	0.958	1.0211	0.9601	702.9
1	81.30	87.34	1.01	705.1	707.6	1.016	2.299	0.854	0.954	1.0230	0.9611	678.2
3	72.12	79.74	0.71	1028.9	1032.1	1.040	2.042	0.792	0.933	1.0338	0.9666	550.5
1	70.71	78.08	0.67	1099.4	1096.4	1.047	1.994	0.780	0.929	1.0359	0.9677	527.3
3	60.99	68.68	0.52	1432.5	1426.7	1.094	1.767	0.720	0.908	1.0471	0.9733	418.7
1	58.93	66.08	0.49	1517.7	1510.0	1.110	1.714	0.705	0.902	1.0499	0.9748	393.8
1	49.90	55.92	0.40	1812.2	1807.0	1.190	1.538	0.653	0.883	1.0600	0.9799	312.4
3	47.42	53.38	0.39	1879.5	1875.0	1.215	1.500	0.641	0.879	1.0624	0.9810	295.1
1	40.97	45.37	0.34	2071.5	2075.1	1.312	1.391	0.608	0.866	1.0693	0.9845	245.7
3	38.35	42.50	0.32	2134.1	2141.2	1.356	1.356	0.597	0.862	1.0716	0.9857	229.7
2	24.74	40.40	0.31	2184.3	2187.7	1.392	1.331	0.589	0.859	1.0732	0.9865	218.4
1	29.68	31.86	0.27	2349.6	2360.4	1.587	1.237	0.561	0.848	1.0792	0.9895	175.3
3	25.57	27.17	0.24	2433.8	2443.8	1.744	1.189	0.547	0.843	1.0821	0.9909	152.9
2	15.93	22.14	0.22	2523.9	2525.4	1.981	1.140	0.534	0.837	1.0850	0.9924	129.5
2	9.80	11.71	0.16	2708.0	2681.9	2.970	1.053	0.510	0.827	1.0905	0.9951	82.5
2	5.32	5.68	0.10	2831.5	2791.5	4.375	1.015	0.493	0.820	1.0943	0.9970	58.3
4	0.00	0.00	0.00	2960.2	2960.2	7.664	1.000	0.467	0.809	1.1003	1.0000	45.4

[a] NRTL parameters: $\tau_{AB} = 0.6416$; $\tau_{BA} = 1.8127$; $\alpha = 0.6987$. [b] NRTL parameters: $\tau_{AB} = 0.6155$; $\tau_{BA} = 1.6534$; $\alpha = 0.7700$.

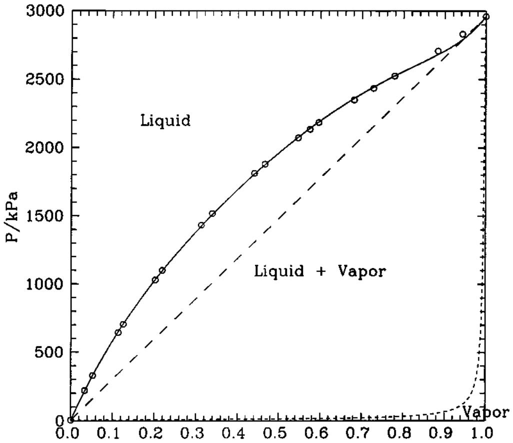

Figure 6. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (- - -), and Raoult's law (— —) for trifluoroacetic acid (A) + hydrogen chloride (B) at 5 °C.

Table 6. Liquid−Liquid Equilibrium Data for Dimethyl Carbonate (A) + Water (B)

	t/°C	mol % A	mol % B
lower liquid	20.0	87.26 ± 0.05	12.74 ± 0.05
upper liquid		2.74 ± 0.01	97.26 ± 0.01
lower liquid	60.0	76.08 ± 0.09	23.92 ± 0.09
upper liquid		3.15 ± 0.02	96.85 ± 0.02

measurements at 60 °C are plotted in Figure 4. This plot shows positive deviation from Raoult's law in the dilute-propane region and negative deviation from Raoult's law in the propane-rich region. The activity coefficients of both compounds have values between 1.5 and 1.9 at the run temperatures. However, significant vapor-phase nonidealities exist for this system, particularly in the propane-rich region at 60 °C. These vapor phase nonidealities account for the shape of the *Px* plot.

4. Dimethyl Ether + Propane. Results of *PTx* measurements on a dimethyl ether + propane system at 0 and 50 °C are reported in Table 4 and the results at 50 °C are plotted in Figure 5. The Wilson activity coefficient equation was used to reduce the data. This system shows positive deviation from Raoult's law.

The *PTx* data indicate the presence of a minimum-boiling azeotrope at both temperatures in the dilute dimethyl ether 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, it should be noted that the chemicals used for these measurements were well degassed prior to initiating the *PTx* runs and additional

Table 7. Solubility Measurement Results of Hydrogen (A) in α-Methyl Benzyl Alcohol (B)

t/°C	P/MPa	$100y_{\mathrm{A}}$[a]	$100x_{\mathrm{A}}$[b]	H/MPa
50.0	3.447	99.997	0.670	514.54
50.0	6.895	99.998	1.332	517.76
50.0	10.342	99.999	1.974	523.83
100.0	3.447	99.939	0.939	366.95
100.0	6.895	99.968	1.863	370.01
100.0	10.342	99.977	2.751	375.89
150.0	3.447	99.445	1.264	271.30
150.0	6.895	99.710	2.505	274.44
150.0	10.342	99.798	3.707	278.39

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

Table 8. Constants Used in the Data Reduction Procedures

compound	MW	T_C/K	P_C/kPa	Z_C	ω	ref
n-butane	58.123	425.12	3796	0.274	0.2002	*a*
tert-butyl mercaptan	90.189	530.0	4060	0.283	0.1914	*a*
dimethyl carbonate	90.079					
dimethyl ether	46.069	400.10	5370	0.274	0.2002	*a*
ethyl mercaptan	62.136	499.15	5490	0.274	0.1921	*a*
hydrogen	2.016	33.18	1313	0.305	−0.2150	*a*
hydrogen chloride	36.461	324.65	8308.7	0.249	0.1322	*a*
α-methyl benzyl alcohol	122.16	673.22	3872	0.239	0.6466	*b*
phenol	94.113	694.25	6130	0.243	0.4259	*a*
propane	44.096	369.83	4248	0.276	0.1523	*a*
styrene	104.152	648.0	4000	0.261	0.2356	*a*
trifluoroacetic acid (monomer)	114.024	487.20	6000	0.163	0.2570	*b*
trifluoroacetic acid (dimer)	228.048	603.70	3006	0.163	0.2923	*b*
water	18.015					

[a] Measured and/or estimated values reported by Daubert et al. (1995). [b] Estimated using techniques shown in Chapter 2 of Reid et al. (1987).

Table 9. Measured and Literature Vapor Pressures

		P/kPa		
compound	t/°C	meas	lit[a]	% dev[b]
n-butane	50	496.3	496.4	−0.04
	100	1525.5	1528.5	−0.19
tert-butyl mercaptan	10	12.32	12.30	0.18
	60	88.27	88.58	−0.35
dimethyl ether	0	266.3	267.4	−0.39
	50	1140.6	1148.4	−0.68
ethyl mercaptan	50	167.6	166.3	0.80
	100	639.9	630.4	1.49
hydrogen chloride	−15	1720.3	1691.4	1.71
	5	2960.2	2912.8	1.63
phenol	60	0.660	0.702	−5.98
	100	5.482	5.430	0.96
propane	0	474.2	474.9	−0.15
	10	635.6	637.3	−0.27
	50	1708.2	1715.1	−0.40
	60	2115.4	2118.4	−0.14
styrene	60	5.137	5.178	−0.79
	100	25.490	25.655	−0.64
trifluoroacetic acid	−15	1.400	1.399	0.07
	5	5.078	5.021	1.14

[a] Literature data calculated from correlations in Daubert et al. (1995). [b] Percent deviation: 100 × (measured − literature)/literature.

degassing was performed throughout the measurements. The carefully measured data show an increase in pressure upon adding small increments of dimethyl ether to propane at both temperatures. These facts strongly suggest the presence of an azeotrope.

Table 10. Source and Purity of Chemicals

compound	CAS no.	supplier	purity, mass %
n-butane	106−97−8	Phillips	99.9+
tert-butyl mercaptan	75−66−1	Aldrich	99.8
dimethyl carbonate	616−38−6	Aldrich	99.9
dimethyl ether	115−10−6	Aldrich	99.9
ethyl mercaptan	75−08−1	Kodak	99.9+
hydrogen	1333−74−0	U. S. Welding	99.99
hydrogen chloride	7647−01−0	Matheson Gas	99.999
α-methyl benzyl alcohol	98−85−1	Aldrich	99.7
phenol	108−95−2	Aldrich	99.9
propane	74−98−6	Phillips	99.9+
styrene	100−42−5	Aldrich	99.8[a]
trifluoroacetic acid	76−05−1	Aldrich	99.9
water	7732−18−5	Mt. Olympus	99.9+

[a] The styrene used for the *PTx* measurements contained 0.1 mass % 4-*tert*-butylcatechol as an inhibitor.

5. Trifluoroacetic Acid + Hydrogen Chloride. *PTx* measurements on trifluoroacetic acid + hydrogen chloride were performed at −15 and +5 °C. The NRTL activity coefficient model was used to reduce the data. Results of the measurements are given in Table 5, and the results of the 5 °C measurements are plotted in Figure 6. This system also shows positive deviation from ideality. Because of the vapor-phase association and the high pressures encountered with this system at these conditions, it is advisable to measure *PTxy* data to verify the equilibrium vapor- and liquid-phase compositions. *PTxy* measurements could also be used to refine the overall model for this system. Such measurements were beyond the scope of this project.

6. Dimethyl Carbonate + Water. The dimethyl carbonate + water system exhibits a region of immiscibility at both 20 and 60 °C. Liquid−liquid equilibrium measurements were performed on this system and are reported in Table 6.

7. α-Methyl Benzyl Alcohol + Hydrogen. Results of the solubility measurements for hydrogen in α-methyl benzyl alcohol at 50, 100, and 150 °C are listed in Table 7. These measurements were made at pressures of 3.45, 6.90, and 10.34 MPa at each of the temperatures. The data show a slight increase in the apparent Henry's constant with an increase in pressure.

Ancillary Data. Table 8 gives the physical constants for each compound used in the data reduction procedures. Table 9 compares the measured pure-component vapor pressures to correlations reported by Daubert et al. (1995). Table 10 lists the source and purity of the chemicals used in this study. The styrene contained 0.1 mass % 4-*tert*-butylcatechol as an inhibitor. The chemicals were degassed before being used whenever possible. Table 10 also lists the Chemical Abstracts Service Registry number for each chemical.

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