1966 *J. Chem. Eng. Data* **2006,** *51,* 1966−1972

Vapor−Liquid Equilibria on Four Binary Systems: 2-Phenylpropionaldehyde + Phenol, Propylene Glycol Monomethyl Ether + Nitroethane, Dimethyl Ether + Propylene, and *N*-Butyric Acid + Propionic Acid[†]

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Vapor−liquid equilibria are reported for the following four systems: 2-phenylpropionaldehyde + phenol at 100 °C and 150 °C; propylene glycol monomethyl ether + nitroethane at 40 °C and 80 °C; dimethyl ether + propylene at −20 °C and 20 °C; and *n*-butyric acid + propionic acid at 100 °C and 140 °C. The system pressure and temperature were measured at several charge compositions along a given isotherm for each system. Equilibrium vapor- and liquid-phase compositions were derived from the measured *PTx* data using the Soave equation of state to represent the vapor phase and the Wilson or three-parameter Redlich−Kister activity coefficient model to represent the liquid phase. Vapor-phase dimerization of the carboxylic acids was accounted for in reducing the *n*-butyric acid + propionic acid *PTx* data. A single *Txy* data point was also measured for this system at each temperature by withdrawing and analyzing multiple samples from the equilibrium vapor and liquid phases.

Introduction

This work is part of an ongoing investigation of phase equilibria for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Properties, DIPPR, of the American Institute of Chemical Engineers. This paper reports measurements that were performed under Project 805/99 and Project 805/00 to obtain vapor−liquid equilibrium (VLE) data on four binary systems. These systems and their measurement temperatures are as follows:

1. 2-Phenylpropionaldehyde + phenol at 100 °C and 150 °C.
2. Propylene glycol monomethyl ether + nitroethane at 40 °C and 80 °C.
3. Dimethyl ether + propylene at −20 °C and 20 °C.
4. *n*-Butyric acid + propionic acid at 100 °C and 140 °C.

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. A *Txy* data point was obtained for *n*-butyric acid + propionic acid (system 4) at each temperature by directly measuring the composition of the equilibrium vapor and liquid phases at a single charge composition. The vapor-phase dimerization of the carboxylic acids was accounted for in the data reduction procedures for this system.

Experimental Section

The apparatus and procedures used for the *PTx* measurements have been described earlier.[1] Temperatures were measured using ITS-90 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 uncertainty of less than ± 0.05 K.

PTx measurements were performed in a glass still apparatus for systems 1, 2, and 4. Pressures measured using this apparatus have an estimated uncertainty of ± 0.03 kPa. A stainless steel apparatus was used to perform the PTx measurements on system 3. Pressures were measured using a calibrated Paroscientific pressure transducer with an estimated uncertainty of ± 0.5 kPa.

The chemicals that are liquid at ambient conditions (2-phenylpropionaldehyde, propylene glycol monomethyl ether, nitroethane, *n*-butyric acid, and propionic acid) were thoroughly degassed prior to the *PTx* measurements. The other chemicals (phenol, dimethyl ether and propylene) were degassed at the beginning of their respective *PTx* measurements. As described in ref 1, the binary mixture was degassed after each chemical addition throughout each *PTx* run.

A stable vapor pressure reading could not be obtained for pure 2-phenylpropionaldehyde at 150 °C (system 1). Therefore, the still was charged with 2-phenylpropionaldehyde and degassed at 100 °C. A small amount of phenol was then added to the still, and the still was heated to 150 °C. Once equilibrium was established at 150 °C, the system was degassed, and a very stable system pressure was measured at a liquid mole fraction of 0.9906 2-phenylpropionaldehyde. The remainder of the run was completed as previously described.[1] The reported vapor pressure of pure 2-phenylpropionaldehyde at 150 °C, 20.97 kPa, was obtained by extrapolating the measured *PTx* data to a mole fraction of 1.0000 2-phenylpropionaldehyde.

Txy measurements on *n*-butyric acid + propionic acid (system 4) were performed using a glass cell apparatus described previously.[1] The cell had an internal volume of about 300 cm^3 and was equipped with vapor and liquid sampling lines. The *Txy* measurements were made by charging the cell with the desired amount of each compound so that the total cell charge

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

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10.1021/je050327l CCC: $33.50

Table 1. *PTx* Measurement Results on 2-Phenylpropionaldehyde (A) + Phenol (B)

				P/kPa								
run	$100z_A$	$100x_A$	$100y_A$	measd	calcd	γ_A	γ_B	φ_A	φ_B	PF_A	PF_B	α_{BA}
						$t = 100\ °C^a$						
1	100.00	100.00	100.00	3.056	3.056	1.000	0.614	0.998	0.999	1.0000	0.9999	1.109
1	94.34	94.34	93.64	3.081	3.077	0.999	0.626	0.998	0.999	1.0000	0.9999	1.132
1	90.06	90.06	88.67	3.097	3.096	0.998	0.639	0.998	0.999	1.0000	0.9999	1.158
1	79.86	79.87	75.99	3.160	3.165	0.986	0.684	0.998	0.999	1.0000	0.9999	1.253
1	69.40	69.40	61.87	3.288	3.286	0.958	0.741	0.998	0.999	1.0000	0.9999	1.398
1	59.66	59.66	48.45	3.456	3.459	0.919	0.800	0.998	0.999	1.0000	0.9999	1.574
2	56.18	56.18	43.78	3.545	3.536	0.902	0.821	0.998	0.999	1.0000	0.9999	1.647
1	49.03	49.04	34.70	3.721	3.723	0.862	0.864	0.998	0.999	1.0000	0.9999	1.811
1	43.82	43.82	28.65	3.877	3.881	0.830	0.892	0.997	0.999	1.0000	1.0000	1.943
2	41.82	41.83	26.50	3.942	3.946	0.817	0.902	0.997	0.998	1.0000	1.0000	1.995
2	31.20	31.22	16.53	4.329	4.323	0.749	0.949	0.997	0.998	1.0001	1.0000	2.291
2	21.18	21.20	9.44	4.709	4.710	0.686	0.979	0.997	0.998	1.0001	1.0000	2.579
2	10.43	10.44	3.91	5.133	5.132	0.628	0.996	0.997	0.998	1.0001	1.0000	2.864
2	5.25	5.25	1.83	5.329	5.331	0.606	0.999	0.997	0.998	1.0001	1.0000	2.980
2	0.00	0.00	0.00	5.529	5.529	0.588	1.000	0.996	0.998	1.0001	1.0000	3.074
						$t = 150\ °C^b$						
1	100.00	100.00	100.00	20.972	20.972	1.000	0.668	0.990	0.995	1.0000	0.9995	1.241
1	99.06	99.06	98.84	21.014	21.020	1.000	0.671	0.990	0.995	1.0000	0.9995	1.247
1	95.02	95.03	93.75	21.244	21.245	0.999	0.685	0.990	0.995	1.0000	0.9995	1.273
1	89.92	89.94	87.21	21.546	21.572	0.997	0.704	0.990	0.995	1.0000	0.9995	1.311
1	79.90	79.92	73.94	22.409	22.387	0.987	0.746	0.989	0.994	1.0001	0.9995	1.403
2	69.81	69.82	60.35	23.491	23.493	0.967	0.792	0.989	0.994	1.0001	0.9996	1.520
1	69.69	69.73	60.23	23.509	23.505	0.967	0.792	0.989	0.994	1.0001	0.9996	1.521
2	64.55	64.57	53.40	24.214	24.199	0.953	0.816	0.989	0.994	1.0001	0.9996	1.590
2	58.51	58.54	45.68	25.118	25.128	0.933	0.844	0.988	0.993	1.0002	0.9996	1.679
2	53.11	53.15	39.11	26.069	26.067	0.912	0.868	0.988	0.993	1.0002	0.9996	1.767
2	42.80	42.87	27.75	28.068	28.141	0.866	0.911	0.987	0.992	1.0003	0.9997	1.954
2	31.93	32.01	17.76	30.779	30.683	0.808	0.950	0.986	0.992	1.0004	0.9998	2.180
2	21.60	21.68	10.26	33.361	33.347	0.748	0.977	0.985	0.991	1.0005	0.9998	2.422
2	10.39	10.44	4.13	36.312	36.378	0.681	0.995	0.984	0.990	1.0007	0.9999	2.709
2	5.52	5.56	2.03	37.616	37.700	0.652	0.999	0.983	0.990	1.0007	1.0000	2.840
2	0.00	0.00	0.00	39.182	39.182	0.619	1.000	0.982	0.989	1.0008	1.0000	2.992

[a] Redlich−Kister parameters: $A = -0.5907$, $B = 0.0217$, $C = 0.0808$. [b] Redlich−Kister parameters: $A = -0.4640$, $B = 0.0381$, $C = 0.0229$.

was about 200 g. After achieving equilibrium at the desired temperature, the system was degassed. The vapor line was further purged by withdrawing additional material through the vapor line into a weighed, evacuated sample vial. Three vapor samples were then withdrawn into weighed, evacuated sample vials. The system was allowed to re-equilibrate to the run temperature between each of the vapor samples. The stirrer was then turned off, and the liquid line was purged. Three liquid samples were then withdrawn into weighed, evacuated sample vials. The mass of each vapor and liquid sample was approximately 1 g.

The vapor and liquid samples were analyzed by gas chromatography (GC). A flame ionization detector was used to quantify the results. Two injections of each sample were made onto the GC column in order to accurately determine the composition of each sample. The average of the analysis results from the three replicate samples from each equilibrium phase was then used to determine the vapor and liquid composition for each run. Individual sample compositions agreed to within ± 0.25 % of the average composition for each result reported in Table 5.

Three calibration standards with compositions ranging from mass fraction of (0.4 to 0.6) *n*-butyric acid in propionic acid were carefully prepared. These standards were analyzed by GC immediately before analyzing the actual samples. The GC response factor that was determined for each calibration standard agreed to within ± 0.3 % of the average of the three standards.

The measured vapor and liquid compositions have an estimated uncertainty of ± 1 % of their reported values. This estimate is based on the agreement between multiple samples taken from the same phase at the same condition and on results obtained by analyzing standards of known composition using the same analytical techniques.

PTx Data Reduction Procedure

The results of the *PTx* measurements, which are total pressure as a function of charge composition at constant temperature, were reduced to equilibrium phase compositions and activity and fugacity coefficients. The Wilson[2] and three-parameter Redlich−Kister[3] activity coefficient models were used to represent the liquid-phase nonidealities. The three-parameter Redlich−Kister expansion did a good job of correlating the results for system 1 while the Wilson equation was used for the other three systems. The Soave−Redlich−Kwong equation of state[4] 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[1] and is similar to the method proposed by Barker.[5] It involves an iterative procedure to solve the following basic equation of VLE:

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

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^o is the vapor pressure of component i at system temperature, ϕ_i^o is the fugacity coefficient of component i at system temperature and corresponding vapor pressure of component i, and the exponential term is the

Table 2. *PTx* Measurement Results on Propylene Glycol Monomethyl Ether (A) + Nitroethane (B)

				P/kPa								
run	$100z_A$	$100x_A$	$100y_A$	measd	calcd	γ_A	γ_B	φ_A	φ_B	PF_A	PF_B	α_{BA}
						$t = 40$ °C[a]						
1	100.00	100.00	100.00	3.614	3.614	1.000	1.935	0.998	0.998	1.0000	0.9999	3.260
1	95.02	95.03	86.01	3.998	3.999	1.001	1.846	0.998	0.998	1.0000	0.9999	3.107
1	90.12	90.13	75.54	4.336	4.335	1.005	1.765	0.998	0.998	1.0000	1.0000	2.958
1	80.00	80.02	60.11	4.921	4.917	1.021	1.611	0.997	0.998	1.0001	1.0000	2.658
1	70.14	70.16	49.77	5.360	5.358	1.050	1.480	0.997	0.998	1.0001	1.0000	2.373
1	60.10	60.11	41.89	5.708	5.702	1.098	1.363	0.997	0.997	1.0001	1.0000	2.091
2	56.59	56.60	39.54	5.789	5.801	1.120	1.326	0.997	0.997	1.0001	1.0000	1.995
2	50.37	50.38	35.73	5.942	5.953	1.167	1.265	0.997	0.997	1.0001	1.0000	1.826
1	49.83	49.84	35.41	5.965	5.965	1.171	1.260	0.997	0.997	1.0001	1.0000	1.812
1	44.77	44.78	32.58	6.065	6.067	1.219	1.215	0.997	0.997	1.0001	1.0000	1.678
2	39.94	39.95	29.99	6.147	6.149	1.275	1.176	0.997	0.997	1.0001	1.0000	1.553
2	30.30	30.31	24.92	6.270	6.270	1.424	1.108	0.997	0.997	1.0001	1.0000	1.310
2	20.20	20.20	19.18	6.339	6.333	1.661	1.052	0.997	0.997	1.0001	1.0000	1.067
2	15.10	15.10	15.79	6.335	6.335	1.829	1.031	0.997	0.997	1.0001	1.0000	0.949
2	10.05	10.05	11.79	6.306	6.307	2.043	1.014	0.997	0.997	1.0001	1.0000	0.836
2	4.98	4.98	6.73	6.241	6.235	2.326	1.004	0.997	0.997	1.0001	1.0000	0.727
2	2.54	2.54	3.71	6.186	6.178	2.495	1.001	0.997	0.997	1.0001	1.0000	0.676
2	0.00	0.00	0.00	6.097	6.097	2.700	1.000	0.997	0.997	1.0001	1.0000	0.624
						$t = 80$ °C[b]						
1	100.00	100.00	100.00	24.179	24.179	1.000	1.700	0.991	0.992	1.0000	0.9998	2.321
1	94.99	95.02	89.54	25.746	25.701	1.001	1.634	0.990	0.992	1.0001	0.9998	2.228
1	90.14	90.19	81.13	27.066	27.022	1.004	1.574	0.990	0.991	1.0001	0.9998	2.140
1	80.02	80.09	67.27	29.352	29.352	1.018	1.459	0.989	0.990	1.0002	0.9999	1.956
1	70.34	70.41	57.15	31.077	31.102	1.041	1.361	0.988	0.990	1.0003	0.9999	1.784
1	59.51	59.56	48.01	32.613	32.594	1.083	1.266	0.988	0.989	1.0003	1.0000	1.595
2	58.12	58.15	46.94	32.715	32.755	1.090	1.254	0.988	0.989	1.0003	1.0000	1.571
2	52.52	52.55	42.89	33.295	33.330	1.121	1.211	0.987	0.989	1.0003	1.0000	1.475
1	49.07	49.10	40.51	33.601	33.633	1.143	1.187	0.987	0.989	1.0003	1.0000	1.417
1	43.84	43.86	37.02	33.972	34.022	1.183	1.152	0.987	0.989	1.0004	1.0000	1.329
2	40.44	40.47	34.81	34.224	34.230	1.213	1.132	0.987	0.989	1.0004	1.0000	1.273
2	31.12	31.13	28.72	34.585	34.622	1.315	1.082	0.987	0.989	1.0004	1.0000	1.122
2	25.83	25.83	25.13	34.790	34.720	1.390	1.058	0.987	0.989	1.0004	1.0000	1.038
2	20.40	20.40	21.18	34.746	34.713	1.484	1.037	0.987	0.989	1.0004	1.0000	0.954
2	15.27	15.26	17.06	34.614	34.585	1.592	1.022	0.987	0.989	1.0004	1.0000	0.875
2	10.13	10.12	12.35	34.307	34.309	1.725	1.010	0.987	0.989	1.0004	1.0000	0.799
2	5.04	5.03	6.81	33.859	33.841	1.887	1.003	0.987	0.989	1.0003	1.0000	0.725
2	0.00	0.00	0.00	33.113	33.113	2.087	1.000	0.987	0.989	1.0003	1.0000	0.654

[a] Wilson equation parameters: $\Lambda_{AB} = 0.3881$, $\Lambda_{BA} = 0.9530$. [b] Wilson equation parameter: $\Lambda_{AB} = 0.4882$, $\Lambda_{BA} = 0.9814$.

Poynting correction where V_i is the molar volume of component i. In the above expression, it is assumed that the molar volume of component i is equal to the partial molar volume of component i at these conditions. Pure component vapor pressures were measured in conjunction with the *PTx* measurements, while pure component molar volumes were calculated from correlations of density data reported in the DIPPR 801 database.[6]

There is an added complexity when working with carboxylic acids because they associate in the vapor phase. This association can be represented by assuming that the organic acid exists as monomer and dimer molecules in equilibrium. The equilibrium constants of propionic acid and *n*-butyric acid were determined from heat of vaporization data and *PVT* data measured previously at Wiltec.[7] These equilibrium constants can be expressed as a function of temperature by the following equation:

$$\log K_p = A + \frac{B}{T/\mathrm{K}} \tag{2}$$

The values of A and B are −10.483 and 3592 for propionic acid and −8.396 and 2729 for *n*-butyric acid. The equilibrium constant in eq 1 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:

$$K_p = \frac{P_{\mathrm{dim}er}}{P_{\mathrm{monomer}}^{\ 2}} \tag{3}$$

A cross-dimer also forms in the vapor between the propionic acid and *n*-butyric acid monomers. The partial pressure of the cross-dimer was estimated to be two times the square root of the product of the partial pressures of the propionic acid and *n*-butyric acid dimers (see pp 138−142 of ref 3).

The data reduction procedure for this system involves solving eq 1 for the monomer of each carboxylic acid. The vapor pressure of each carboxylic acid monomer is taken as its partial pressure over the pure liquid carboxylic acid at the temperature of interest.

Results and Discussion

The results of the phase equilibrium measurements are described below. The *PTx* data are presented in Tables 1 through 4. These tables give the run numbers, the charge compositions (z_A), the calculated liquid (x_A) and vapor (y_A) compositions, the measured and correlated pressures, the activity (γ_A and γ_B) and fugacity coefficients (φ_A and φ_B), the Poynting corrections (PF_A and PF_B), and the relative volatilities (α_{BA}) of the lighter compound (B) over the heavier compound (A). The compositions are reported on a mole basis. The activity coefficient parameters used in the correlation are given 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.

Table 3. *PTx* Measurement Results on Dimethyl Ether (A) + Propylene (B)

				P/kPa								
run	$100z_A$	$100x_A$	$100y_A$	measd	calcd	γ_A	γ_B	φ_A	φ_B	PF_A	PF_B	α_{BA}
					$t = -20$ °C[a]							
1	100.00	100.00	100.00	125.0	125.0	1.000	1.240	0.970	0.973	1.0000	0.9937	2.906
1	93.58	93.66	83.88	140.5	140.3	1.001	1.213	0.966	0.970	1.0005	0.9942	2.841
1	85.07	85.22	67.68	159.5	159.6	1.004	1.180	0.961	0.966	1.0010	0.9949	2.753
1	77.17	77.35	56.12	176.3	176.5	1.010	1.151	0.957	0.962	1.0016	0.9955	2.670
1	67.50	67.66	44.92	195.5	196.1	1.021	1.119	0.953	0.958	1.0022	0.9961	2.565
2	61.58	61.65	39.14	208.0	207.6	1.030	1.101	0.950	0.956	1.0025	0.9965	2.500
1	56.26	56.39	34.62	217.0	217.9	1.040	1.086	0.947	0.954	1.0028	0.9969	2.441
2	56.10	56.20	34.47	218.4	217.6	1.040	1.085	0.947	0.954	1.0028	0.9969	2.439
1	46.75	46.83	27.40	233.9	234.1	1.063	1.061	0.943	0.950	1.0033	0.9975	2.334
2	46.24	46.38	27.08	234.8	234.9	1.064	1.060	0.943	0.950	1.0033	0.9975	2.329
1	41.30	41.34	23.68	243.0	243.4	1.079	1.048	0.941	0.948	1.0036	0.9978	2.272
2	35.54	35.71	20.11	252.8	252.7	1.098	1.037	0.939	0.946	1.0039	0.9981	2.207
2	24.86	25.01	13.81	269.8	269.6	1.143	1.019	0.935	0.943	1.0044	0.9987	2.082
2	13.06	13.17	7.25	287.6	287.7	1.209	1.006	0.931	0.939	1.0049	0.9993	1.941
2	5.23	5.27	2.93	299.5	299.4	1.265	1.001	0.928	0.936	1.0053	0.9997	1.846
2	0.00	0.00	0.00	307.2	307.2	1.309	1.000	0.926	0.935	1.0055	1.0000	1.782
					$t = 20$ °C[b]							
1	100.00	100.00	100.00	508.1	508.1	1.000	1.210	0.918	0.929	1.0000	0.9830	2.195
1	93.58	93.76	87.52	549.2	549.4	1.001	1.184	0.912	0.923	1.0012	0.9844	2.145
1	85.07	85.40	73.79	601.6	601.8	1.004	1.152	0.903	0.915	1.0027	0.9861	2.078
1	77.17	77.56	63.15	648.1	648.3	1.009	1.125	0.896	0.909	1.0040	0.9877	2.016
1	67.50	67.86	52.09	702.2	702.5	1.020	1.095	0.887	0.901	1.0055	0.9895	1.942
2	61.58	61.71	45.95	735.8	735.2	1.028	1.079	0.882	0.896	1.0065	0.9906	1.896
1	56.26	56.52	41.17	761.5	761.9	1.036	1.066	0.878	0.893	1.0072	0.9915	1.857
2	56.10	56.29	40.97	763.2	763.1	1.037	1.066	0.877	0.892	1.0073	0.9915	1.856
1	46.75	46.89	33.07	809.6	809.6	1.055	1.046	0.870	0.886	1.0086	0.9931	1.787
2	46.24	46.53	32.78	811.3	811.3	1.056	1.045	0.870	0.886	1.0087	0.9931	1.784
1	41.30	41.36	28.76	834.9	835.9	1.068	1.036	0.866	0.882	1.0094	0.9939	1.747
2	35.54	35.89	24.68	861.2	861.4	1.083	1.027	0.862	0.879	1.0101	0.9948	1.709
2	24.86	25.20	17.08	909.8	909.5	1.116	1.013	0.854	0.872	1.0115	0.9964	1.635
2	13.06	13.30	8.98	960.5	960.9	1.161	1.004	0.846	0.865	1.0130	0.9981	1.554
2	5.23	5.33	3.62	993.9	994.1	1.197	1.001	0.841	0.860	1.0139	0.9993	1.502
2	0.00	0.00	0.00	1015.9	1015.9	1.224	1.000	0.837	0.857	1.0146	1.0000	1.467

[a] Wilson equation parameters: $\Lambda_{AB} = 0.6945$, $\Lambda_{BA} = 1.0950$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.8513$, $\Lambda_{BA} = 0.9586$.

The results of the measured *Txy* data for system 4 are shown in Table 5. This table shows the measured temperature, the measured liquid and vapor composition on a mole basis, the vapor composition determined from the correlation, and the relative volatility of propionic acid over *n*-butyric acid obtained from the measured data and from the correlation. The correlated values were obtained at the measured liquid compositions using the Wilson equation parameters and the dimerization constants shown in Table 4.

2-Phenylpropionaldehyde + Phenol. The results of the *PTx* measurements on 2-phenylpropionaldehyde + phenol at 100 °C and 150 °C are given in Table 1. The three-parameter Redlich−Kister 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 1 to illustrate the data. This system exhibits negative deviation from ideality with infinite dilution activity coefficients in the range of about 0.6 to 0.7 for both compounds at these temperatures.

Propylene Glycol Monomethyl Ether + Nitroethane. *PTx* measurements on propylene glycol monomethyl ether + nitroethane were performed at 40 °C and 80 °C. The Wilson activity coefficient equation was used to reduce the measured data. The results of these measurements are shown in Table 2. Figure 2 plots the system pressure as a function of the liquid and vapor compositions at 40 °C. This system exhibits positive deviation from ideality, and the measured *PTx* data indicate that a minimum boiling azeotrope is present at a mole fraction of about 0.82 nitroethane at 40 °C and at a mole fraction of about 0.78 nitroethane at 80 °C.

Dimethyl Ether + Propylene. The results of the *PTx* measurements on dimethyl ether + propylene at −20 °C and 20 °C are given in Table 3. The Wilson activity coefficient equation was used to reduce the measured data. The system pressure as a function of liquid and vapor composition at −20 °C is plotted in Figure 3 to illustrate the data. This system exhibits slight positive deviation from ideality with infinite dilution activity coefficients in the range of about 1.2 to 1.3 for both compounds at these temperatures. *PTx* data reported on this system in 1984 by Preuss and Moerke[8] at 15 °C, 25 °C, and 35 °C agree well with the data reported here.

n-Butyric Acid + Propionic Acid. *PTx* measurements on *n*-butyric acid + propionic acid were performed at 100 °C and 140 °C. The Wilson activity coefficient equation was used to reduce the measured data. The results of these measurements are shown in Table 4. Figure 4 shows a plot of the system pressure as a function of the liquid and vapor compositions at 100 °C.

The vapor-phase association of the acids was accounted for in the data reduction procedures and the equilibrium constant of each acid was determined from heat of vaporization data and *PVT* data that were previously measured by Wiltec.[7] A cross-dimer also forms in the vapor between the monomers of propionic acid and *n*-butyric acid. The partial pressure of the cross-dimer was estimated to be two times the square root of the product of the partial pressures of the propionic acid and *n*-butyric acid dimers. The activity coefficients obtained from reducing the measured *PTx* data are close to unity with infinite dilution values ranging from about 1.04 to 1.16 for both compounds at these temperatures.

A single *Txy* measurement was also performed at each temperature at a liquid mole fraction of approximately (0.56 to 0.57) *n*-butyric acid. The results of these measurements are

Table 4. *PTx* Measurement Results on *n*-Butyric Acid (A) + Propionic Acid (B)[a]

				P/kPa								
run	$100z_A$	$100x_A$	$100y_A$	measd	calcd	γ_A	γ_B	φ_A	φ_B	PF_A	PF_B	α_{BA}
					$t = 100$ °C[b]							
1	100.00	100.00	100.00	9.38	9.38	1.000	1.037	0.998	0.999	1.0000	0.9996	1.892
1	95.00	95.00	90.91	9.91	9.96	1.000	1.038	0.998	0.999	1.0000	0.9996	1.900
1	90.04	90.05	82.59	10.55	10.55	1.000	1.038	0.998	0.999	1.0000	0.9997	1.907
1	80.67	80.68	68.54	11.66	11.71	1.000	1.038	0.997	0.999	1.0001	0.9997	1.917
1	70.64	70.65	55.58	13.03	13.04	1.000	1.036	0.997	0.998	1.0001	0.9997	1.924
1	60.21	60.22	44.03	14.43	14.49	1.002	1.033	0.997	0.998	1.0002	0.9998	1.925
2	52.15	52.20	36.25	15.76	15.64	1.005	1.030	0.996	0.998	1.0002	0.9998	1.920
1	49.94	49.95	34.22	15.98	15.97	1.006	1.029	0.996	0.998	1.0002	0.9998	1.918
1	44.52	44.53	29.59	16.72	16.77	1.009	1.026	0.996	0.998	1.0002	0.9998	1.910
2	41.60	41.66	27.27	17.31	17.19	1.011	1.024	0.996	0.998	1.0003	0.9998	1.905
2	30.89	30.95	19.29	18.72	18.79	1.024	1.017	0.995	0.997	1.0003	0.9999	1.875
2	20.11	20.16	12.16	20.40	20.41	1.047	1.009	0.995	0.997	1.0004	0.9999	1.825
2	10.07	10.10	6.02	21.84	21.90	1.086	1.003	0.995	0.997	1.0004	1.0000	1.753
2	5.05	5.07	3.03	22.63	22.64	1.116	1.001	0.995	0.997	1.0004	1.0000	1.705
2	0.00	0.00	0.00	23.38	23.38	1.156	1.000	0.994	0.997	1.0004	1.0000	1.646
					$t = 140$ °C[c]							
1	100.00	100.00	100.00	45.85	45.85	1.000	1.026	0.992	0.996	1.0000	0.9987	1.733
1	94.97	95.02	91.67	47.88	48.14	1.000	1.026	0.992	0.996	1.0001	0.9988	1.732
1	89.81	89.91	83.73	50.37	50.52	1.000	1.025	0.991	0.995	1.0001	0.9989	1.730
1	79.45	79.60	69.33	55.21	55.44	1.000	1.023	0.990	0.995	1.0003	0.9990	1.726
1	69.21	69.39	56.86	60.25	60.44	1.001	1.020	0.989	0.994	1.0004	0.9991	1.720
1	58.83	59.01	45.69	65.53	65.65	1.003	1.017	0.988	0.993	1.0006	0.9992	1.711
2	57.88	58.00	44.68	66.52	66.16	1.003	1.017	0.988	0.993	1.0006	0.9992	1.710
2	52.51	52.65	39.48	69.33	68.88	1.005	1.015	0.987	0.993	1.0007	0.9993	1.704
1	48.29	48.44	35.60	70.86	71.04	1.006	1.014	0.987	0.992	1.0008	0.9994	1.699
1	42.91	43.04	30.87	73.58	73.82	1.008	1.012	0.986	0.992	1.0009	0.9994	1.692
2	42.23	42.40	30.33	74.41	74.15	1.009	1.012	0.986	0.992	1.0009	0.9994	1.691
2	31.63	31.81	21.81	79.66	79.65	1.015	1.008	0.985	0.991	1.0010	0.9996	1.673
2	20.50	20.67	13.65	85.28	85.46	1.026	1.004	0.984	0.991	1.0012	0.9997	1.647
2	10.27	10.37	6.68	90.87	90.85	1.042	1.001	0.983	0.990	1.0014	0.9999	1.617
2	5.17	5.23	3.33	93.58	93.54	1.053	1.000	0.983	0.990	1.0015	0.9999	1.599
2	0.00	0.00	0.00	96.29	96.29	1.067	1.000	0.982	0.989	1.0015	1.0000	1.578

[a] Values for the dimerization constants of propionic acid and *n*-butryic acid were obtained from ref 7. These constants, in units of kPa^{-1}, can be expressed as a function of temperature by the following equation: $\log K_P = A + B/(T/\mathrm{K})$. The values of A and B are −10.483 and 3592 for propionic acid and −8.396 and 2729 for *n*-butyric acid. The partial pressure of the cross-dimer was estimated to be two times the square root of the product of the partial pressures of the propionic acid and *n*-butyric acid dimers. [b] Wilson equation parameters: $\Lambda_{AB} = 0.4211$, $\Lambda_{BA} = 1.7201$. [c] Wilson equation parameters: $\Lambda_{AB} = 0.5686$, $\Lambda_{BA} = 1.5001$.

Table 5. *PTxy* Measurements on the *n*-Butyric Acid (A) + Propionic Acid (B) Binary System[a]

t	$100x_A$	$100y_A$		α_{BA}	
°C	measured	measured	correlation	measured	correlation
100	56.58	41.30	40.39	1.852	1.923
140	55.88	42.98	42.58	1.680	1.707

[a] The correlated values were obtained at the measured liquid composition using the Wilson equation parameters and the dimerization constants shown in Table 4.

shown in Table 5. The relative volatility of propionic acid over *n*-butyric acid obtained from the measured *Txy* data is approximately 3.8 % lower than the corresponding value obtained from the *PTx* correlation at 100 °C. The measured relative volatility at 140 °C is about 1.6 % lower than the corresponding value obtained from the *PTx* correlation. Additional *Txy* data are recommended in order to better define the VLE behavior of this system, especially at low concentrations of each acid.

Data have been reported in the literature on this system after the measurements reported here were performed in 2000. Miyamoto et al.[9] reported isothermal *PTxy* data at 85 °C in 2001. The following year, Sewnarain et al.[10] reported isobaric *PTxy* data at 14 kPa. The relative volatility of propionic acid over *n*-butyric acid of 1.95 at 14 kPa and 100 °C reported by Sewnarain agrees well with the value of 1.93 obtained using the *PTx* correlation at 100 °C shown in Table 4.

Table 6. Constants Used in Data Reduction Procedure

compound	MW	T_C/K	P_C/kPa	Z_C	ω	footnote
2-phenylpropionaldehyde	134.178	682	3300	0.247	0.4589	*a*
phenol	94.113	694.25	6130	0.243	0.4435	*a*
propylene glycol monomethyl ether	90.122	579.8	4113	0.242	0.4427	*a*
nitroethane	75.067	593	5160	0.247	0.3803	*a*
dimethyl ether	46.069	400.10	5370	0.274	0.2002	*a*
propylene	42.081	364.85	4600	0.281	0.1376	*a*
n-butyric acid monomer	88.106	538.0	4060	0.266	0.315	*b*
n-butyric acid dimer	176.212	710.0	2280	0.253	0.480	*b*
propionic acid monomer	74.079	508.4	4740	0.268	0.283	*b*
propionic acid dimer	148.158	657.9	2810	0.259	0.403	*b*
n-butyric acid + propionic acid cross-dimer	162.185	666.0	2670	0.256	0.418	*c*

[a] Measured and/or estimated values reported in ref 6. [b] Reported in ref 7. [c] Critical properties of the cross-dimer were estimated to be the same as those of 1-ethyl-2-isopropyl benzene reported in ref 6.

Table 7. Measured and Literature Vapor Pressures

		P/kPa		
compound	*t*/°C	measd	lit[a]	% dev[b]
2-phenylpropionaldehyde	100	3.056	4.982 ± 10 %[c]	−38.7
	150	20.97	27.24 ± 10 %[c]	−23.0
phenol	100	5.529	5.518 ± 3 %	0.2
	150	39.18	38.91 ± 3 %	0.7
propylene glycol monomethyl ether	40	3.614	3.759 ± 10 %	−2.6
	80	24.18	24.22 ± 10 %	−0.2
nitroethane	40	6.097	6.053 ± 5 %	0.7
	80	33.11	33.27 ± 5 %	−0.5
dimethyl ether	−20	125.0	124.5 ± 5 %	+0.4
	20	508.1	512.9 ± 5 %	−0.9
propylene	−20	307.2	309.8 ± 3 %	−0.8
	20	1015.9	1030.4 ± 3 %	−1.4
n-butyric acid	100	9.38	9.41 ± 5 %	−0.3
	140	45.85	46.73 ± 5 %	−1.9
propionic acid	100	23.38	23.57 ± 3 %	−0.8
	140	96.29	97.74 ± 3 %	−1.5
allyl alcohol	30	4.29	4.58 ± 5 %	−6.3
	55	16.81	17.54 ± 5 %	−4.2
propionaldehyde	30	49.78	51.98 ± 3 %	−4.2
	55	124.4	128.4 ± 3 %	−3.1

[a] See vapor pressure correlations in ref 6. [b] Percent deviation: 100 × (measured − literature)/literature. [c] Experimental vapor pressure data and the accompanying correlation reported in ref 11 give a vapor pressure for 2-phenylpropionaldehyde of 3.084 kPa at 100 °C and 20.80 kPa at 150 °C.

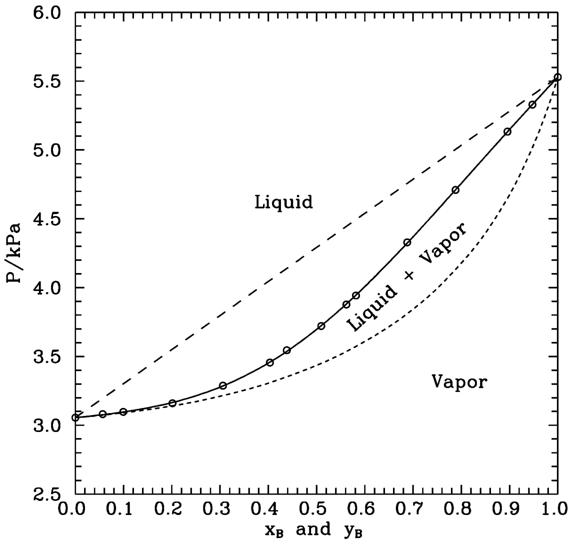

Figure 1. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and — —, Raoult's law for 2-phenylpropionaldehyde (A) + phenol (B) at 100 °C.

The isothermal *PTxy* data reported by Miyamoto at 85 °C suggest that the relative volatility only changes slightly with composition over the entire composition range. This is contrary to the results obtained using the *PTx* correlation at 100 °C shown in Table 4. Here the relative volatility varies from 1.892 at the pure *n*-butyric acid end to a maximum of about 1.925 at a mole fraction of about 0.4 propionic acid, and then drops to 1.646 at the pure propionic acid end. This change in the relative volatility as a function of composition is not as pronounced in the *PTx* correlation at 140 °C. The reported correlations for this complex system have an estimated uncertainty of ± 10 % in the relative volatility. As previously mentioned, additional *Txy* data at 100

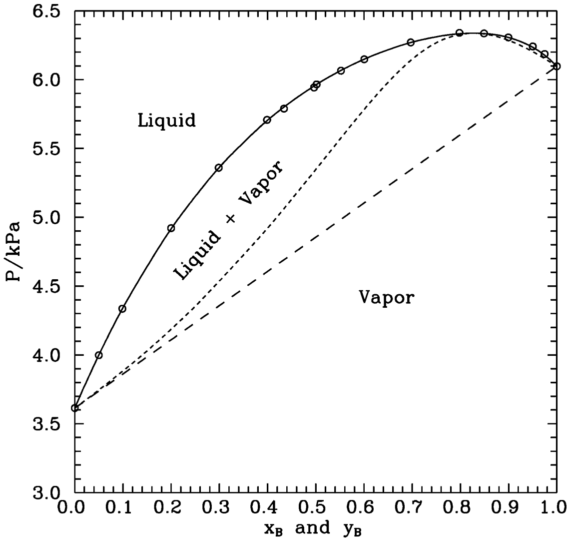

Figure 2. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and — —, Raoult's law for propylene glycol monomethyl ether (A) + nitroethane (B) at 40 °C.

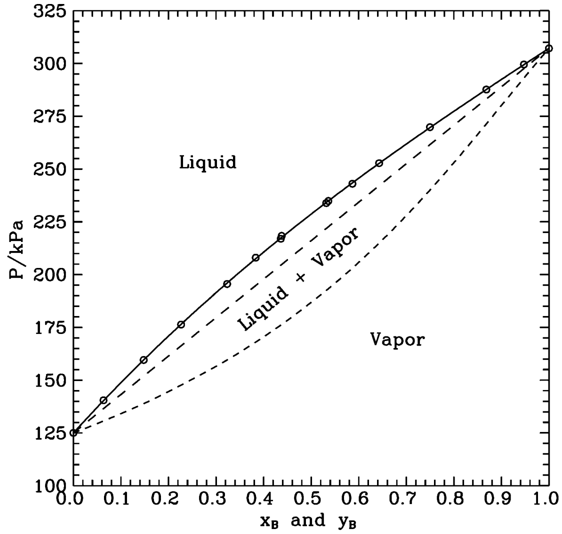

Figure 3. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and — —, Raoult's law for dimethyl ether (A) + propylene (B) at −20 °C.

Table 8. Source and Purity of Chemicals

			mass fraction purity	
compound	CASRN	supplier	Wiltec analysis	Supplier analysis
2-phenylpropionaldehyde	93-53-8	Lancaster	0.987	0.994
phenol	108-95-2	Aldrich	0.999+	0.999
propylene glycol monomethyl ether	107-98-2	Aldrich	0.993	0.997
nitroethane	79-24-3	Aldrich	0.998	0.998
dimethyl ether	115-10-6	Aldrich	0.999+	0.999
propylene	115-07-1	Matheson	0.999+	0.995+[a]
n-butyric acid	107-92-6	Aldrich	0.999	0.999
propionic acid	79-09-4	Aldrich	0.999	0.999

[a] This is a product specification and not an actual lot analysis.

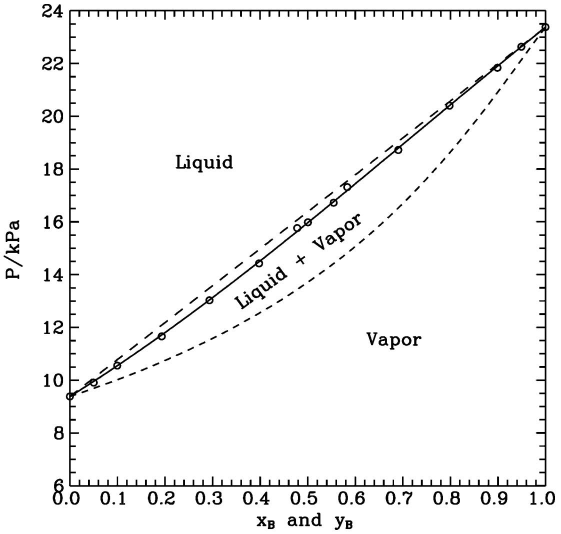

Figure 4. ○, measured *PTx* data; —, *P*−*x* correlation; - - -, *P*−*y* correlation; and — —, Raoult's law for *n*-butyric acid (A) + propionic acid (B) at 100 °C.

°C and 140 °C are recommended if greater accuracy is required, especially at low concentrations of each acid.

Ancillary Data. Table 6 gives the physical constants for each compound used in the *PTx* data reduction procedure. Table 7 compares the measured pure component vapor pressures to correlations reported in the DIPPR 801 database.[6] Table 8 lists the Chemical Abstracts Service Registry number together with the source and purity of each chemical used in this study.

Acknowledgment

We thank Mark B. Swenson, Merril R. Chipman, and Matthew E. Mainord, who helped measure the experimental data.

Literature Cited

(1) Giles, N. F.; Wilson, H. L.; Wilding, W. V. Phase equilibrium measurements on twelve binary mixtures. *J. Chem. Eng. Data* **1996**, *41*, 1223−1238.

(2) Wilson, G. M. Vapor−liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

(3) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1986.

(4) Soave, G. Equilibrium constants from a modified Redlich−Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.

(5) Barker, J. A. Determination of activity coefficients from total pressure measurements. *Aust. J. Chem.* **1953**, *6*, 207−210.

(6) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Yang, Y.; Zundel, N. A. *DIPPR Data Compilation of Pure Chemical Properties*; Design Institute for Physical Properties, AIChE: New York, 2005.

(7) Jasperson, L. V.; Wilson, L. C.; Brady, C. J.; Wilding, W. V.; Wilson, G. M. *Experimental Results from the Design Institute for Physical Property Data*; AIChE Symposium Series 271; AIChE: New York, 1989; pp 102−139.

(8) Preuss, H.; Moerke, K. Determination of the VLE in the binary systems of dimethyl ether with propene, methane and 2-methylpropane. *FIZ Rep.* **1984**, *No. 11141*.

(9) Miyamoto, S.; Nakamura, S.; Iwai, Y.; Arai, Y. Measurement of isothermal vapor−liquid equilibria for monocarboxylic acid + monocarboxylic acid binary systems with a flow-type apparatus. *J. Chem. Eng. Data* **2001**, *46*, 405−409.

(10) Sewnarain, R.; Ramjugernath, D.; Raal, J. D. Isobaric vapor−liquid equilibria for the systems propionic acid + butyric acid, isobutyric acid + butyric acid, butyric acid + isovaleric acid, and butyric acid + hexanoic acid at 14 kPa. *J. Chem. Eng. Data* **2002**, *47*, 603−607.

(11) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Measurements of vapor pressure, heat capacity, and density along the saturation line for cyclopropane carboxylic acid, *N*,*N*-diethylethanolamine, 2,3-dihydrofuran, 5-hexen-2-one, perfluorobutanoic acid, and 2-phenylpropionaldehyde. *J. Chem. Eng. Data* **2002**, *47*, 715−724.

Received for review August 15, 2005. Accepted December 21, 2005. We are grateful to the DIPPR 805 steering committee and to the companies it represents for funding this research.

JE050327L