Total Pressure Measurements of Binary Mixtures Containing *tert*-Amyl Methyl Ether and *tert*-Amyl Alcohol

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The vapor pressure of pure *tert*-amyl methyl ether (TAME) was measured together with isothermal $P-x$ data for mixtures of pentane + TAME and pentane + *tert*-amyl alcohol (TAOH) at temperatures between 70 and 110 °C. Also, activity coefficients at infinite dilution for the binary mixtures of TAME + TAOH were obtained in the 90–120 °C temperature range. The $P-T-x$ data were correlated using the Peng–Robinson equation of state separately with the van der Waals and Wong–Sandler mixing rules.

Introduction

Vapor–liquid equilibrium data are needed for the reformulation of gasoline to meet Federal Clear Air Act standards. Oxygenates, such as ethers and alcohols, are known to reduce CO emissions from motor vehicles, and ethers are used as a substitute for aromatics in gasoline to improve the octane rating. In this study the total pressures above binary mixtures of pentane with *tert*-amyl methyl ether (TAME) and *tert*-amyl alcohol (TAOH) were measured in a static equilibrium apparatus at temperatures between 70 and 110 °C over the entire composition range. The activity coefficients at infinite dilution for the binary TAME and TAOH system were also obtained in the temperature range of 90–120 °C. These data were correlated using the Stryjek-Vera (*1*) version of the Peng-Robinson (*2*) equation of state. The classical van der Waals mixing rules and also the Wong–Sandler (*3*) mixing rules with the Wilson (*4*) and UNIQUAC (*5*) models for the excess Gibbs free energy were used to correlate these data.

Experimental Measurements

Materials. TAME from Aldrich Chemical Co. was dried over type 4A molecular sieves, and then fractionally distilled on a 100 theoretical plate column at a reflux ratio of not less than 30:1. From a gas chromatographic analysis (FID and TCD) we found that the purity was approximately 99.8 mass %. TAOH, obtained from Aldrich, was also dried over sieves and then distilled, resulting in a purity of about 99.8%. Pentane (Aldrich) had a purity above 99.8%, and was used as received.

Apparatus and Procedure. The experimental data were obtained in the static still apparatus shown in Figure 1. This apparatus, designed to measure the total pressure of mixtures at temperatures to 120 °C and pressures to 750 kPa, consisted of two similar units. Each included a temperature bath and a static cell which was connected to a pressure transducer and a vacuum pump. One unit, used for degassing of pure substances, was placed in a water bath thermostat and equipped with an absolute pressure transducer, MKS Model 128AA-01000, with measuring range 0–1000 Torr. The second unit, used for the measurements of the total pressure of the binary mixtures, was immersed in a silicon oil temperature bath, and was equipped with a pressure transducer which had a range of 0–10000 Torr of absolute pressure. These transducers were calibrated by measuring the vapor pressure of very high purity pentane. These transducers have a reported

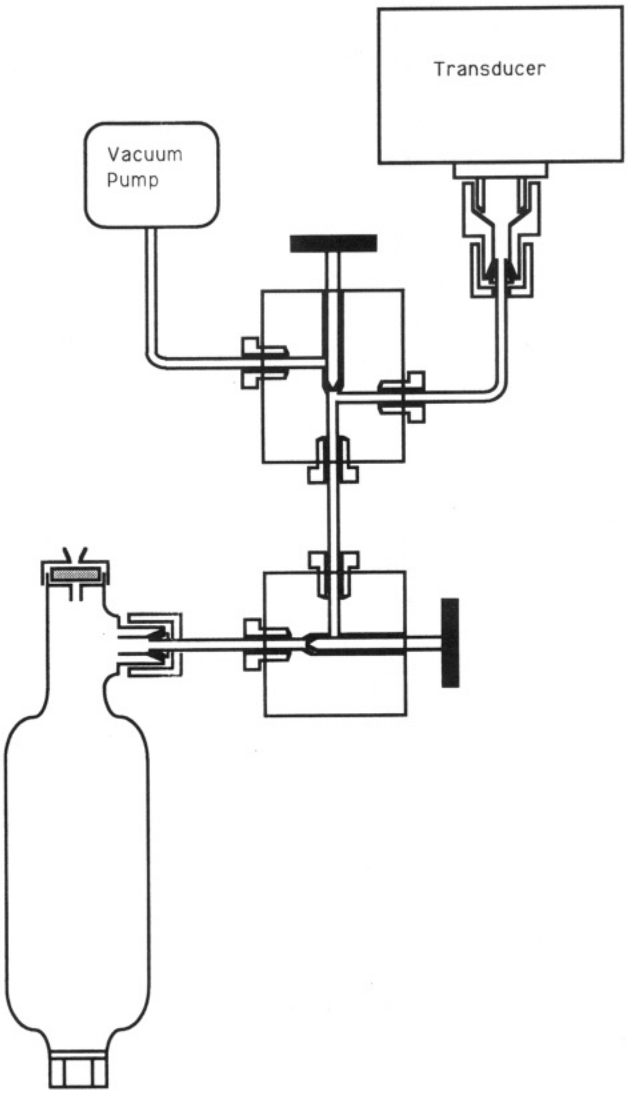

Figure 1. Diagram of the static cell used in the measurements reported here.

accuracy of 0.25% of the reading, and we estimate our pressure readings are accurate to about 0.35%.

Both transducers and tubing connections were heated above the cell temperatures to avoid condensation within the pressure measuring part of the apparatus. The temperature of the oil bath was monitored by a Fluke digital thermometer with an accuracy of 0.01 K, and was controlled within 0.05 K. Other temperatures were monitored with type J thermocouples.

The metal stainless steel cell used in the measurements had a volume of 50 cm^3, and was equipped with an injection port and a needle valve so that the cell could be attached to a vacuum line or the pressure transducer using an HIP three-way valve. The connections were similar to those described by Bennett et al. (*6*). During the measurements the glass static cell described in that work was also used as a degassing cell.

The chemicals used in the experiments were degassed as follows. The cell filled with the compound was submerged into liquid nitrogen, and then evacuated for 10 min. Next the cell was placed in a water bath of fixed temperature, the chemical melted and agitated above the melting temperature, and its vapor pressure measured. This freeze–evacuation procedure was repeated several times; usually three or four cycles were sufficient for proper degassing, as determined by agreement between measured vapor pressures and those reported in the literature, and the fact that the measured vapor pressure did not change on additional freeze–evacuation–thaw procedures. After degassing, the amount of component remaining was determined by weighing the cell on a balance which had an accuracy of 0.1 mg.

Following degassing, the cell and its contents (the solvent) were kept at a temperature so that the solute vapor pressure would be close to atmospheric pressure to ensure no leakage of air into the cell. The stainless steel cell with the gravimetrically determined amount of the component was then connected to the second unit of the system where the pressure of the binary mixture is measured. The addition of the second component (the solute), which had also been degassed in the manner described above, was then made by weighed injections through the injection port. Once stable temperature and pressure readings were obtained, the total pressure was recorded. Further solute additions were then made until measurements had been made over the concentration range from 0 to approximately 60 mol % solute. The cell was then emptied, and measurements were made reversing the roles of solvent and solute.

To obtain the activity coefficients at infinite dilution for the binary TAME + TAOH mixture, the same procedure was used, only many, much smaller solute injections were made, covering the concentration range from 0 to 6 mol % solute. We estimate the error in these measurements to be less than 0.0005 in mole fraction.

Results and Correlation

Vapor Pressure of Pure Components. Vapor pressure data for pentane and TAOH at temperatures up to 120 °C were obtained from the TRC data bank (*7*). Literature data for TAME at temperatures higher than 86 °C were not available. The vapor pressure of TAME was obtained in this work over the temperature range from 65 to 125 °C using the static cell apparatus, and these data are collected in Table 1. Good agreement was found between our measurements and literature values (*8*) in 65–89 °C temperature range.

Table 1. Pure Vapor Pressure of TAME from 338.36 to 398.08 K

T/K	P/kPa	T/K	P/kPa
338.36	51.200	377.07	165.30
342.48	58.800	377.43	166.70
347.19	68.700	377.91	169.30
350.12	75.500	380.99	183.10
353.66	84.500	381.23	184.00
357.91	96.200	381.40	185.40
362.19	109.10	384.11	198.90
362.32	109.70	384.50	200.40
364.42	116.30	385.68	206.20
366.89	125.00	386.47	210.50
367.14	126.10	386.94	213.90
369.62	134.80	387.52	215.60
371.95	144.30	389.72	229.10
372.19	144.60	392.10	242.80
372.22	144.80	394.65	258.10
373.79	151.90	396.27	268.20
374.84	155.50	398.08	280.40

Table 2. Antoine Equation Coefficients for TAME, TAOH, and Pentane

	Antoine constants			
component	*A*	*B*	*t*/°C	AAD(*P*)^a/kPa
TAME	6.069 411	1280.109	65–125	0.183
TAOH	5.643 784	863.245	25–122	0.000
pentane	6.122 655	1150.422	54–110	0.000

^{a} Absolute average deviation in pressure.

Table 3. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.0720, A_{12} = −775.0 J mol^{-1}, and A_{21} = 1003.8 J mol^{-1}) for Pentane (1) + TAOH (2) at 70 °C

$x_{2(\text{tot})}$	$x_{2(\text{calc})}$	$y_{2(\text{calc})}$	*P*(meas)/kPa	*P*(calc)/kPa
0.000	0.000	0.000	282.9	281.2
0.057	0.058	0.024	277.4	276.2
0.116	0.118	0.036	269.4	269.6
0.163	0.166	0.043	263.7	263.9
0.209	0.213	0.049	258.0	258.0
0.253	0.257	0.055	251.9	252.1
0.291	0.295	0.059	247.0	246.7
0.357	0.362	0.068	236.8	236.7
0.387	0.392	0.072	231.9	231.9
0.413	0.418	0.075	227.8	227.5
0.439	0.443	0.079	223.5	223.2
0.462	0.466	0.082	219.0	218.9
0.503	0.507	0.089	211.1	211.1
0.538	0.541	0.095	204.3	204.1
0.400	0.403	0.073	230.4	230.1
0.432	0.436	0.078	224.5	224.4
0.450	0.454	0.080	221.1	221.2
0.469	0.474	0.083	217.4	217.6
0.489	0.495	0.087	213.1	213.5
0.512	0.518	0.091	208.6	208.8
0.537	0.544	0.095	203.1	203.5
0.565	0.573	0.101	196.9	197.1
0.631	0.640	0.116	180.4	180.6
0.669	0.678	0.128	169.7	169.9
0.711	0.721	0.143	156.9	156.8
0.759	0.770	0.166	140.4	140.4
0.814	0.824	0.203	119.8	119.5
0.876	0.884	0.275	92.6	92.3
0.947	0.951	0.466	57.2	57.1
1.000	1.000	1.000	27.4	27.5

The vapor pressure data for the components studied here were correlated using the Antoine equation

$$\log(P/\text{kPa}) = A + B/(C + t/{}^\circ\text{C}) \tag{1}$$

and the constants we obtained are reported in Table 2.

Total Pressure of Binary Mixtures. The total pressures of binary mixtures of pentane with TAME and of pentane with TAOH have been measured over the entire composi-

Table 4. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.0680, A_{12} = 108.1 J mol^{-1}, and A_{21} = 224.2 J mol^{-1}) for Pentane (1) + TAOH (2) at 90 °C

$x_{2(tot)}$	$x_{2(calc)}$	$y_{2(calc)}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	470.4	468.2
0.049	0.050	0.027	463.7	460.6
0.117	0.121	0.049	448.7	447.0
0.177	0.183	0.063	433.5	433.8
0.228	0.235	0.074	422.2	422.1
0.275	0.282	0.083	410.6	411.0
0.316	0.323	0.091	401.0	400.9
0.351	0.358	0.097	391.9	391.9
0.382	0.389	0.103	383.7	383.7
0.411	0.418	0.109	375.7	375.6
0.437	0.444	0.115	367.6	368.3
0.462	0.469	0.120	362.5	361.0
0.483	0.490	0.125	355.3	354.5
0.504	0.510	0.129	349.0	348.0
0.523	0.529	0.134	344.3	341.9
0.541	0.546	0.139	337.8	335.9
0.406	0.410	0.107	377.5	378.1
0.420	0.424	0.110	373.0	374.1
0.451	0.456	0.117	364.5	364.9
0.468	0.473	0.121	359.4	359.6
0.487	0.493	0.125	353.8	353.5
0.507	0.514	0.130	346.8	346.8
0.529	0.537	0.136	339.2	339.1
0.553	0.562	0.143	330.3	330.5
0.580	0.589	0.150	320.5	320.7
0.608	0.618	0.160	309.2	309.2
0.641	0.652	0.172	295.3	295.4
0.676	0.687	0.186	278.8	279.6
0.715	0.727	0.206	260.0	260.5
0.758	0.771	0.234	236.8	237.2
0.808	0.820	0.276	207.6	207.6
0.864	0.874	0.348	171.4	170.9
0.929	0.936	0.502	124.3	123.3
1.000	1.000	1.000	64.9	64.4

tion range at temperatures of 70, 90, and 110 °C. These data are listed in Tables 3–8, which give both the total mole fraction of the oxygenate and the liquid mole fraction after correction for partial volatization as described below. This vaporization correction was generally less than 0.006 mole fraction. Figure 2 shows isotherms for the pentane + TAME mixture.

For the TAME in TAOH mixture the total pressures were measured at temperatures of 90, 105, and 120 °C in the concentration range of 0–0.045 mole fraction TAME. For the TAOH in TAME mixture, total pressure data were obtained at temperatures of 90, 100, 105, and 120 °C in the concentration range of 0–0.065 mole fraction TAOH. These data are reported in Tables 9–15.

Modeling Data Using a Cubic Equation of State. The components and mixtures studied here are of interest to the petroleum industry for the reformulation of gasoline. Equations of state are the traditional method of describing mixtures in this industry, and for this reason we use an equation of state here. In particular, we used the Peng–Robinson (*2*) equation of state with the modification proposed by Stryjek and Vera (*1*) in order to obtain accurate pure component vapor pressures. The PRSV equation is

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2} \tag{2}$$

$$a = (0.457235R^2T_c^{\,2}/P_c)\alpha \tag{3}$$

$$b = 0.077796RT_c/P_c \tag{4}$$

Table 5. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.0690, A_{12} = −2432.5 J mol^{-1}, and A_{21} = 3703.6 J mol^{-1}) for Pentane (1) + TAOH (2) at 110 °C

$x_{2(tot)}$	$x_{2(calc)}$	$y_{2(calc)}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	737.0	736.2
0.056	0.058	0.032	717.7	717.3
0.113	0.117	0.056	696.4	696.6
0.163	0.168	0.074	678.2	677.9
0.208	0.214	0.088	660.9	661.0
0.248	0.255	0.099	645.6	645.5
0.285	0.292	0.109	631.5	631.2
0.318	0.326	0.118	618.3	618.2
0.348	0.356	0.126	605.9	606.0
0.376	0.383	0.134	594.9	594.6
0.401	0.408	0.141	584.4	583.9
0.424	0.430	0.147	574.4	574.1
0.446	0.452	0.153	564.7	564.3
0.466	0.472	0.159	555.5	555.2
0.484	0.490	0.165	546.8	546.4
0.502	0.507	0.170	538.7	537.9
0.518	0.523	0.176	530.9	529.8
0.534	0.538	0.181	523.7	522.0
0.401	0.405	0.140	579.1	585.2
0.414	0.420	0.144	572.6	578.9
0.429	0.435	0.148	567.5	572.0
0.445	0.452	0.153	561.4	564.5
0.462	0.470	0.159	551.3	556.1
0.481	0.489	0.165	542.8	546.9
0.501	0.510	0.171	532.0	536.6
0.523	0.533	0.179	521.6	525.0
0.547	0.558	0.188	508.7	511.7
0.573	0.585	0.199	493.8	496.5
0.602	0.615	0.211	476.9	478.9
0.633	0.648	0.227	457.0	458.7
0.668	0.684	0.246	433.5	434.8
0.708	0.724	0.272	405.9	405.9
0.753	0.769	0.308	372.2	371.1
0.804	0.819	0.361	329.9	328.1
0.860	0.873	0.444	279.6	276.7
0.927	0.935	0.608	213.8	210.7
1.000	1.000	1.000	133.2	133.2

with

$$\alpha = [1 + k(1 - T_R^{\,0.5})]^2 \tag{5}$$

$$\kappa = \kappa_0 + \kappa_1(1 + T_R^{\,0.5})(0.7 - T_R) \tag{6}$$

and

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{7}$$

where T_c, P_c, and ω are, respectively, the critical temperature, critical pressure, and acentric factor of the pure substance, R is the gas constant, V is the molar volume, and P is the pressure. Also $T_R = T/T_c$ is the reduced temperature, and κ_1 is a substance specific parameter adjusted to give accurate vapor pressures.

Two sets of equation of state mixing rules were used. The first were the classical van der Waals mixing rules

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{8}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{9}$$

with the combining rules

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \quad \text{and} \quad b_{ij} = (b_i + b_j)/2 \tag{10}$$

where k_{ij} is the binary interaction parameter adjusted to give a good fit of experimental data. These mixing and combining rules are not expected to give a good fit of alcohol

Table 6. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model ($k_{12} = -0.0020$, $A_{12} = 8924.9$ J mol^{-1}, and $A_{21} = 371.8$ J mol^{-1}) for Pentane (1) + TAME (2) at 70 °C

$x_{2(\text{tot})}$	$x_{2(\text{calc})}$	$y_{2(\text{calc})}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	283.5	281.6
0.063	0.064	0.019	268.9	267.5
0.122	0.125	0.037	255.2	254.5
0.162	0.177	0.054	245.5	243.7
0.219	0.223	0.069	234.6	234.0
0.262	0.266	0.085	225.4	225.0
0.300	0.304	0.099	217.4	217.1
0.335	0.339	0.112	209.9	209.7
0.367	0.371	0.126	203.0	203.1
0.395	0.399	0.138	197.1	197.3
0.417	0.421	0.148	192.6	192.7
0.438	0.441	0.158	187.8	188.4
0.457	0.460	0.167	183.9	184.4
0.478	0.482	0.178	179.8	179.9
0.498	0.501	0.189	175.5	175.7
0.515	0.518	0.198	171.7	172.1
0.375	0.377	0.128	202.1	201.9
0.390	0.393	0.135	198.7	198.6
0.407	0.409	0.143	195.5	195.1
0.425	0.428	0.151	191.1	191.2
0.445	0.448	0.161	187.2	187.0
0.466	0.470	0.172	182.0	182.3
0.490	0.494	0.185	177.4	177.2
0.517	0.521	0.200	171.6	171.4
0.546	0.551	0.218	165.0	165.1
0.579	0.584	0.240	157.6	157.9
0.616	0.621	0.267	149.8	149.7
0.658	0.664	0.301	140.2	140.3
0.707	0.712	0.347	129.4	129.4
0.763	0.769	0.412	116.7	116.5
0.829	0.834	0.509	101.6	101.2
0.907	0.910	0.672	83.2	82.8
1.000	1.000	1.000	60.4	60.4

Table 7. Calculations Using the PSRV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model ($k_{12} = 0.0038$, $A_{12} = 7563.2$ J mol^{-1}, and $A_{21} = 467.1$ J mol^{-1}) for Pentane (1) + TAME (2) at 90 °C

$x_{2(\text{tot})}$	$x_{2(\text{calc})}$	$y_{2(\text{calc})}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	469.9	468.2
0.059	0.061	0.021	448.5	446.7
0.112	0.116	0.040	428.6	427.5
0.161	0.166	0.058	410.4	410.5
0.205	0.210	0.075	395.3	395.4
0.245	0.251	0.091	381.0	381.9
0.281	0.286	0.106	368.5	369.9
0.314	0.319	0.120	357.8	358.9
0.344	0.349	0.133	347.1	349.0
0.371	0.376	0.145	337.2	339.8
0.396	0.401	0.157	328.8	331.4
0.420	0.424	0.169	320.8	323.5
0.442	0.446	0.180	313.1	316.2
0.462	0.466	0.191	306.4	309.5
0.481	0.484	0.202	300.2	303.1
0.498	0.502	0.212	294.0	297.2
0.373	0.382	0.148	339.0	337.8
0.386	0.396	0.155	334.2	333.1
0.401	0.411	0.162	329.3	328.1
0.417	0.427	0.170	323.8	322.6
0.433	0.444	0.179	317.6	316.8
0.452	0.463	0.190	311.1	310.4
0.472	0.483	0.201	304.2	303.5
0.493	0.505	0.214	296.4	295.9
0.517	0.530	0.229	287.8	287.6
0.544	0.556	0.247	278.5	278.3
0.573	0.586	0.268	268.0	268.0
0.605	0.618	0.292	256.4	256.5
0.641	0.655	0.323	243.7	243.6
0.682	0.696	0.361	228.8	228.9
0.729	0.741	0.411	211.9	212.1
0.782	0.793	0.479	192.8	192.8
0.843	0.853	0.576	170.3	170.2
0.915	0.921	0.727	143.9	143.7
1.000	1.000	1.000	112.2	111.9

+ hydrocarbon mixtures. The second set of mixing rules used were those recently proposed by Wong–Sandler (*3*) which are given below

$$b_{\mathrm{m}} = Q/(1 - D) \tag{11}$$

$$\frac{a_{\mathrm{m}}}{RT} = Q\frac{D}{(1 - D)} \tag{12}$$

$$Q = \sum_i \sum_j x_i x_j (b - a/RT)_{ij} \tag{13}$$

with

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{(b_i - a_i/RT) + (b_j - a_j/RT)}{2}(1 - k_{ij}) \tag{14}$$

and

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{A^{\mathrm{ex}}}{cRT} \tag{15}$$

where c is a constant equal to $[1/\sqrt{2}]\ \ln(\sqrt{2} - 1)$ for the PRSV equation, and A^{ex} is any suitable molar excess Helmholtz free energy model at infinite pressure or equivalently an excess Gibbs free energy model at low pressures (Wong et al. (*3*)). The Wilson (*4*) activity coefficient model

$$A^{\mathrm{ex}} = -RT\sum_i x_i \ln\left(\sum_j x_j \Lambda_{ij}\right) \tag{16}$$

with

$$\Lambda_{ij} = \frac{V_i}{V_j}\exp\left(-\frac{A_{ij}}{RT}\right) \tag{17}$$

where V_i is the liquid molar volume of species i, was used here with the parameters reported in the data tables. The properties of the components under investigation are collected in Table 16 together with the sources of these data. The values of the parameter κ_1 were computed from our data. Since there were no reliable values in the literature for the acentric factors of TAME and TAOH, these were also calculated from our vapor pressure data.

Correction of the Measured Mixture Data for Partial Vaporization. The tubing and pressure transducer used in our measurements have a significant dead volume (12.82 cm^3), and our cells cannot be completely filled initially because large quantities of solute must be added. This coupled with the fact that our measurements are above ambient pressure (so that the mass in the vapor phase cannot be ignored) means that the liquid composition in our static cell is slightly changed from that of the gravimetrically prepared feed. The following procedure was used to account for this small concentration change.

From the measured volume of our cells (52.90 and 53.63 cm^3 for the two cells we used), the connecting tubing, and transducers and the liquid densities of the components, we could compute the liquid and vapor volumes in the equipment for each loading (assuming no liquid vaporization). We then used the PRSV equation of state with both sets of mixing rules discussed above and a set of mixing and combining rule parameters to calculate the vapor composition and density that would be in equilibrium with this liquid. Then, using a mass balance, we recomputed the liquid composition and volume, and the vapor phase properties. This iterative calculation was repeated three or four times, until the vapor and liquid compositions no longer changed. The calculation was then repeated to

Table 8. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.0820, A_{12} = 5267.7 J mol^{-1}, and A_{21} = − 205.6 J mol^{-1}) for Pentane (1) + TAME (2) at 110 °C

$x_{2(tot)}$	$x_{2(calc)}$	$y_{2(calc)}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	737.9	736.2
0.058	0.062	0.024	703.6	701.4
0.110	0.115	0.045	673.8	671.5
0.154	0.161	0.064	648.8	646.7
0.196	0.204	0.082	624.8	623.7
0.235	0.244	0.099	603.3	602.5
0.271	0.279	0.116	584.9	583.7
0.303	0.311	0.131	567.6	566.8
0.332	0.340	0.145	551.5	551.5
0.361	0.369	0.161	536.8	536.3
0.388	0.395	0.175	522.3	522.7
0.412	0.419	0.188	510.1	510.0
0.435	0.442	0.202	498.3	498.2
0.456	0.463	0.214	487.0	487.3
0.476	0.482	0.227	476.3	477.1
0.495	0.500	0.238	467.6	467.7
0.369	0.372	0.162	533.0	534.6
0.382	0.385	0.169	525.9	527.8
0.396	0.399	0.177	519.2	520.5
0.410	0.414	0.185	512.0	512.6
0.426	0.431	0.195	503.4	504.0
0.443	0.448	0.205	494.5	494.9
0.462	0.467	0.217	484.7	484.9
0.482	0.488	0.230	474.3	474.2
0.503	0.510	0.245	462.6	462.6
0.528	0.535	0.262	449.7	449.6
0.554	0.562	0.282	435.8	435.5
0.583	0.591	0.305	420.0	419.9
0.616	0.624	0.333	402.1	402.5
0.652	0.661	0.366	383.2	383.1
0.692	0.702	0.407	361.6	361.7
0.738	0.747	0.459	337.5	337.5
0.790	0.798	0.526	309.5	310.0
0.849	0.857	0.620	277.7	278.0
0.919	0.924	0.761	240.5	239.9
1.000	1.000	1.000	193.9	193.8

optimize the choice of mixing and combining rule parameters. In the tables we report the gravimetrically determined overall composition, the measured pressure, the calculated vapor and liquid compositions, and the calculated pressure. As can be seen in the tables, the difference between the gravimetrically prepared composition and the calculated liquid composition is never more than 0.01 mole fraction, and usually considerably less than this.

The results of the binary mixture correlation, as average percent deviation in pressure, for the pentane + TAME and pentane + TAOH mixtures are reported in Table 17. It is evident that while a good description of the pentane + TAME system is obtained with either mixing rule, the pentane + TAOH binary mixture is not accurately described using the van der Waals mixing rule. However, good results are obtained for this system with the Wong–Sandler mixing rule. As an example, results of the correlations for the pentane + TAOH system at 90 °C are shown in Figure 3. Similar results were observed at the other temperatures.

Activity Coefficients at Infinite Dilution. The activity coefficients at infinite dilution were calculated from our isothermal $P-x$ data of TAME in TAOH and TAOH in TAME mixtures using the following expression given by Van Ness and Abbott (*9*):

$$\gamma_i^\infty = \frac{\phi_i^\infty}{P_i^{\mathrm{vap}}}\left(P_j^{\mathrm{vap}} + \Delta Z_j^{\mathrm{VL}} \lim_{x_i \to 0}\left(\frac{\partial P}{\partial x_i}\right)_T\right) \qquad (18)$$

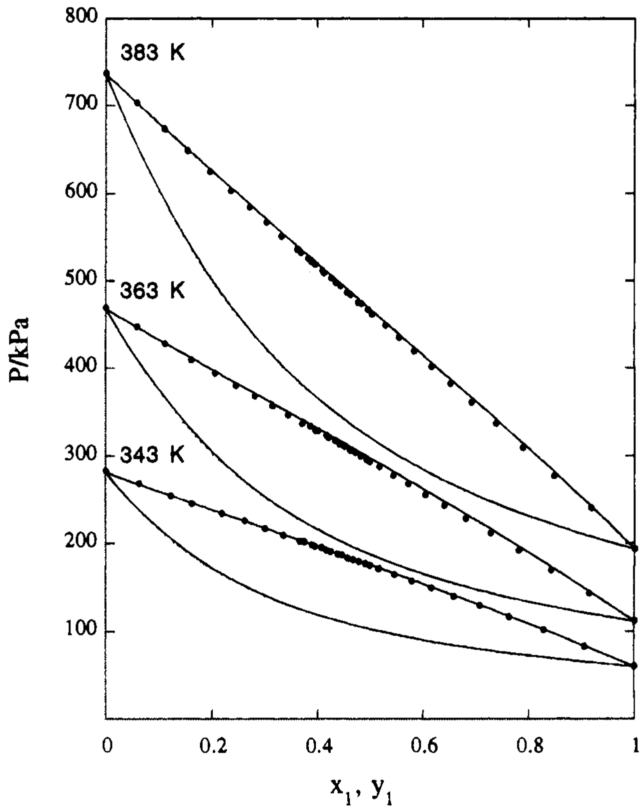

Figure 2. TAME (1) + pentane (2) at 343, 363, and 383 K. Points are the experimental data; lines are the equation of state correlation with the Wong–Sandler mixing rules.

Table 9. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.0090, A_{12} = 4344.2 J mol^{-1}, and A_{21} = − 1524.0 J mol^{-1}) for TAME (1) in TAOH (2) at 90 °C

$x_{1(tot)}$	$x_{1(calc)}$	$y_{1(calc)}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	64.9	64.9
0.005	0.005	0.013	65.4	65.5
0.012	0.012	0.031	66.1	66.2
0.019	0.019	0.047	66.9	66.9
0.026	0.025	0.061	67.4	67.5
0.032	0.032	0.075	68.1	68.1
0.038	0.038	0.087	68.7	68.7
0.045	0.045	0.100	69.3	69.2

Table 10. Calculations Using the PRSV Equation of state with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.0098, A_{12}=1064.8 J mol^{-1}, and A_{21} = 512.2 J mol^{-1}) for TAME (1) in TAOH (2) at 105 °C

$x_{1(tot)}$	$x_{1(calc)}$	$y_{1(calc)}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	112.5	112.4
0.006	0.006	0.012	113.2	113.2
0.013	0.013	0.026	114.0	114.1
0.019	0.019	0.039	114.8	114.9
0.025	0.025	0.050	115.7	115.6
0.031	0.030	0.061	116.2	116.3
0.036	0.036	0.071	117.0	117.0
0.040	0.040	0.079	117.5	117.5

Here γ_i^∞ is the infinite dilution activity coefficient of species i in species j, P_i^{vap} is a pure component vapor pressure, $\Delta Z_j^{\mathrm{VL}} = Z_j^{\mathrm{V}} - Z_j^{\mathrm{L}}$ is the difference between the vapor and liquid compressibility factors, and $\lim_{x_i \to 0}(\partial P/\partial x_i)_T$ is the measured initial slope of the change in pressure with liquid composition. In our measurements this limiting slope ranged from 0.10 to 0.17 kPa/mole fraction for TAME in TAOH at the temperatures studied with a correlation coefficient for a linear fit over the whole composition range

Table 11. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.0009, A_{12} = −1232.4 J mol^{-1}, and A_{21} = 4921.3 J mol^{-1}) for TAME (1) in TAOH (2) at 120 °C

$x_{1(\mathrm{tot})}$	$x_{1(\mathrm{calc})}$	$y_{1(\mathrm{calc})}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	182.9	182.9
0.009	0.009	0.016	184.7	184.4
0.016	0.015	0.029	185.7	185.6
0.022	0.022	0.041	186.9	186.8
0.030	0.029	0.054	188.0	188.0
0.036	0.036	0.065	189.1	189.1

Table 12. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.5000, A_{12} = −4660.2 J mol^{-1}, and A_{21} = 7689.9 J mol^{-1}) for TAOH (1) in TAME (2) at 90 °C

$x_{1(\mathrm{tot})}$	$x_{1(\mathrm{calc})}$	$y_{1(\mathrm{calc})}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	112.2	112.1
0.012	0.012	0.010	111.9	112.0
0.023	0.023	0.021	111.9	111.8
0.035	0.035	0.030	111.7	111.7
0.046	0.046	0.040	111.4	111.5
0.057	0.057	0.049	111.3	111.3

Table 13. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.2500, A_{12} = −2414.5 J mol^{-1}, and A_{21} = 1896.4 J mol^{-1}) for TAOH (1) in TAME (1) at 100 °C

$x_{1(\mathrm{tot})}$	$x_{1(\mathrm{calc})}$	$y_{1(\mathrm{calc})}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	148.6	148.6
0.009	0.009	0.007	148.2	148.3
0.018	0.018	0.014	148.0	148.0
0.027	0.027	0.021	147.7	147.7

Table 14. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.0100, A_{12} = 1777.1 J mol^{-1}, and A_{21} = − 698.9 J mol^{-1}) for TAOH (1) in TAME (2) at 105 °C

$x_{1(\mathrm{tot})}$	$x_{1(\mathrm{calc})}$	$y_{1(\mathrm{calc})}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	170.1	170.0
0.012	0.012	0.010	169.7	169.7
0.023	0.023	0.020	169.4	169.4
0.034	0.034	0.029	168.9	169.1
0.045	0.045	0.038	168.8	168.8
0.056	0.056	0.047	168.5	168.5

Table 15. Calculations Using the PRSV Equation of State with the Wong–Sandler Mixing Rule and the Wilson Activity Coefficient Model (k_{12} = 0.0135, A_{12} = −884.6 J mol^{-1}, and A_{21} = 6902.8 J mol^{-1}) for TAOH (1) in TAME (2) at 120 °C

$x_{1(\mathrm{tot})}$	$x_{1(\mathrm{calc})}$	$y_{1(\mathrm{calc})}$	P(meas)/kPa	P(calc)/kPa
0.000	0.000	0.000	248.9	248.8
0.012	0.012	0.012	248.7	248.8
0.023	0.023	0.023	248.9	248.9
0.034	0.034	0.034	248.8	248.9
0.045	0.045	0.045	248.9	248.9
0.055	0.055	0.055	249.0	248.9
0.065	0.065	0.065	248.8	248.9

Table 16. Properties of TAME, TAOH, and Pentane used in Equation of State Calculations

component	T_c/K	P_c/bar	ω	ref	κ_1	V/(cm^3 mol^{-1})
TAME	531.2	32.53	0.3565	3	−0.1907	132.7
TAOH	545.0	39.50	0.4965	11	0.4549	109.5
pentane	469.7	33.69	0.2543	12	−0.0022	115.26

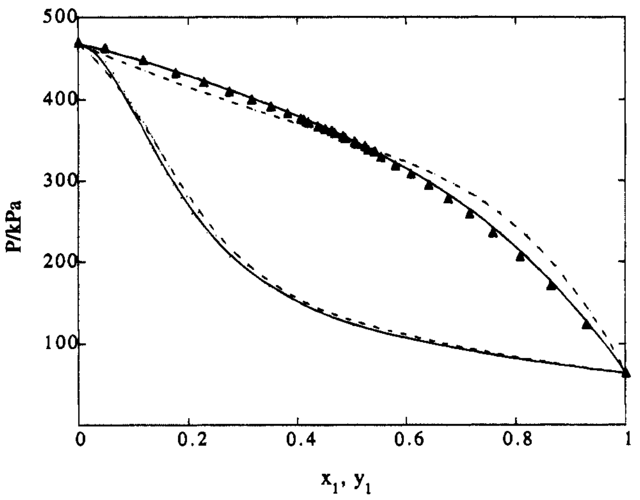

Figure 3. TAOH (1) + pentane (2) at 363 K. Points are the experimental data; lines are the equation of state correlation: the solid line is the correlation with the Wong–Sandler mixing rules, and the dashed line is the correlation with the van der Waals mixing rules.

Table 17. Correlation of Pentane + TAOH and Pentane + TAME Mixtures

system	T/K	av % dev in pressure	
		vdW	WS–Wilson
pentane + TAOH	343.16	4.258 (k_{12} = 0.0126)	0.133
	363.16	2.905 (k_{12} = 0.0150)	0.200
	383.16	1.616 (k_{12} = 0.0118)	0.335
pentane + TAME	343.10	0.213 (k_{12} = 0.0815)	0.208
	343.16	0.367 (k_{12} = 0.0853)	0.364
	383.16	0.181 (k_{12} = 0.0796)	0.136

Table 18. Second Virial Coefficients for TAOH (1) and TAME (2)

T/K	B_1/(cm^3 mol^{-1})	B_2/(cm^3 mol^{-1})	B_{12}/(cm^3 mol^{-1})
363.15	−1633	−1303	−859
373.15	−1437	−1206	−792
378.15	−1353	−1162	−761
393.15	−1144	−1044	−681

Table 19. Calculated Infinite Dilution Activity Coefficients for the TAOH (1) + TAME (2) System

T/K	γ_1^∞	γ_2^∞	T/K	γ_1^∞	γ_2^∞
363.15	1.53	1.51	378.15	1.31	1.45
373.15	1.28		393.15	1.42	1.47

of our measurements of 0.999. For TAOH in TAME this limiting slope ranged from 0.00 to −0.03 over the temperature range. Assuming the liquid phase can be described by the virial equation truncated at the second virial coefficient, we have

$$\Delta Z_j^{\mathrm{VL}} = Z_j^{\mathrm{V}} - Z_j^{\mathrm{L}} = 1 + (P_j^{\mathrm{vap}}/RT)(B_{ij} - V_j^{\mathrm{L}}) \quad (19)$$

and

$$\phi_i^\infty = \exp\left(\frac{(B_{ii} - V_i^{\mathrm{L}})(P_j^{\mathrm{vap}} - P_i^{\mathrm{vap}}) + P_j^{\mathrm{vap}}(2B_{ij} - B_{ii} - B_{jj})}{RT}\right) \quad (20)$$

where B_{ij} is the cross second virial coefficient for a binary mixture of species i and j. In this work, the virial coefficients have been calculated by the method of Tsonopoulos (*10*), and the values are collected in Table 18. The activity coefficients at infinite dilution are listed in Table 19.

Conclusions

The $P-T-x$ vapor–liquid equilibrium data are reported for the pentane + TAOH and pentane + TAME binary mixtures over the entire composition range. Data from which activity coefficients at infinite dilution can be computed for the binary TAME + TAOH mixture are also reported, together with pure component vapor pressures for TAME at temperatures to 125 °C. The analysis of these data with a cubic equation of state shows that the vapor–liquid equilibrium data for the TAME + pentane mixture can be easily correlated using the PRSV equation of state and the van der Waals mixing rules. These mixing rules cannot describe the data for the pentane + TAOH mixture very accurately, and produce an average deviation in pressure of up to 4.5%. However, the deviation in the correlation with the Wong–Sandler mixing rule is less than 1% when either the Wilson or UNIQUAC excess free energy model is used.

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