

Total Pressure Measurements for Pentane + Methanol + Ethanol at 303.15 K

Jay L. Reimers, Venkat R. Bhethanabotla, and Scott W. Campbell*

Department of Chemical Engineering, University of South Florida, Tampa, Florida 33620-5350

Total pressure is reported as a function of liquid-phase composition for pentane + methanol + ethanol at 303.15 K. The data were reduced using Barker's method. The excess Gibbs energy of the liquid phase is represented by a rational function obtained by making an empirical modification to the nonrandom two-liquid (NRTL) equation. The resulting fit to the data is superior to that obtained using a previous representation based on a modified Margules equation.

Introduction

As part of a continuing study of vapor-liquid equilibrium in ternary systems that contain two associating species, total pressure measurements are reported here for pentane + methanol + ethanol at 303.15 K. These data supplement those for ethanol + heptane + isobutanol (1) and pentane + methanol + 2-butanol (2) reported earlier. Total pressure measurements are also reported here for pentane + ethanol, and for methanol + ethanol, at 303.15 K. Data for the third constituent binary system of this study, pentane + methanol, were reported earlier (2).

Experimental Section

Apparatus and Procedure. The apparatus and procedure are identical to those used in previous studies (1, 2). The isothermal cell is of the Van Ness type (3) into which measured volumes of the components are charged and the pressure is recorded. Overall cell composition is determined from the volumetric data using saturated liquid densities from the literature. Saturated densities at room temperature were obtained for *n*-pentane from ref 4 and for methanol and ethanol from ref 5.

For binary systems, each of the two piston injectors is filled with a pure compound. For ternary measurements, one injector is filled with a pure compound and the other filled with a mixture of the other two components. In this work, pure *n*-pentane was charged to one piston injector and mixtures of methanol and ethanol were charged to the other. Excess volume data given by Benson (6) were used with the room-temperature saturated liquid densities of the pure components to obtain the density of the methanol-ethanol mixtures in the piston injector. The methanol + ethanol mixtures in the piston injector were characterized by the parameter C'

$$C' = \frac{z_2}{z_2 + z_3} \quad (1)$$

where z_2 and z_3 are the overall mole fractions of methanol and ethanol in the equilibrium cell. Values for C' of 0.2627, 0.5061, and 0.7584 were examined in this work.

Experimental data consists of pressure as a function of the overall mole fractions in the equilibrium cell. Corrections to obtain the exact liquid-phase composition are made as part of

the data reduction procedure, as described earlier (1, 2). Experimental uncertainties are $\pm 0.1\%$ in pressure, ± 0.02 K in temperature, and between ± 0.0005 and ± 0.001 in liquid phase mole fraction, the smaller number applying toward the extremes in composition.

Materials. The chemicals were of the same grade, and from the same suppliers, as those used in previous investigations (1, 2). Methanol and *n*-pentane (HPLC grade) were purchased from Aldrich Chemical and had minimum purities of 99.97 and 99.5%, respectively. Ethanol was obtained from Aaper Alcohol and Chemical and had a minimum purity of 99.9%. All chemicals were degassed as described earlier (1). No further purification was attempted.

An indication of the purity of the chemicals used is given by a comparison of the measured vapor pressures with previously measured values. The vapor pressure for methanol was measured as part of the methanol + ethanol binary measurements, and a value of 21.85 kPa was obtained. This is in good agreement with the value of 21.88 kPa measured earlier (2) as part of the pentane + methanol study. The vapor pressure of ethanol was measured twice: once for the methanol + ethanol binary and once for the pentane + ethanol binary. The measured values of 10.47 and 10.51 kPa, respectively, are in good agreement with the average value of 10.46 kPa reported previously (1). Because of the manner in which the ternary measurements were made, the vapor pressure of *n*-pentane was measured five times. Values ranged between 81.97 and 82.07 kPa with an average of 82.03 kPa. This is also in agreement with the previously reported value of 82.01 kPa (2).

Data Reduction. Data reduction proceeded by Barker's method (7), as described earlier (1, 2). Unweighted regressions were performed in which the sum of the squares of the differences between the measured and calculated pressures were minimized. In the present work, a new model for the excess Gibbs energy of the liquid phase was applied. In earlier work (1, 2), the approach outlined by Abbott et al. (8) was used in which it was assumed that G^E of the ternary system is given by the sum of all of the binary G^E functions plus a contribution containing ternary terms. The excess Gibbs energies of the binary systems were represented by a modified Margules equation and a ten-parameter function was used for the ternary contribution. This function did not prove adequate for the system examined here since the regressions converged to a parameter set that introduced a pole in the denominator of one of the ternary terms.

Although it would be possible to eliminate this difficulty by choosing a different empirical form for the ternary function, the search for an appropriate model is tedious and a new model developed by Campbell (9) was used instead. This model assumes that the excess Gibbs energy is given by an empirical modification of the nonrandom two-liquid (NRTL) (10) model:

$$G^E/RT = \sum_i x_i \left(\sum_j \tau_{ji} G_{ji} x_j / \sum_k G_{ki} x_k \right) \quad (2)$$

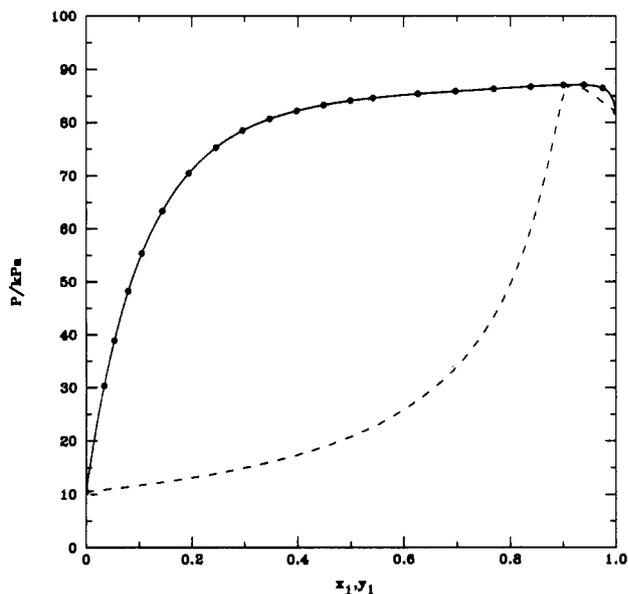
The modification allows the parameters G_{ij} to depend on composition according to

$$G_{ij} = \sum_k \frac{1}{a_{kij} x_k} \quad (3)$$

* To whom correspondence should be addressed.

Table I. Saturated Liquid Volumes V_i^L and Second Molar Virial Coefficients B_{ij} Used for Pentane (1) + Methanol (2) + Ethanol (3) at 303.15 K

	<i>n</i> -pentane	methanol	ethanol
$V_i^L/(\text{cm}^3 \text{ mol}^{-1})$	117.1	41.0	58.9
$B_{ii}/(\text{cm}^3 \text{ mol}^{-1})$	-1172	-1840	-2600
$B_{12}/(\text{cm}^3 \text{ mol}^{-1}) = -666$ $B_{13}/(\text{cm}^3 \text{ mol}^{-1}) = -765$			
$B_{23}/(\text{cm}^3 \text{ mol}^{-1}) = -2200$			

**Figure 1.** Pressure P vs liquid-phase mole fraction x_1 , or vapor-phase mole fraction y_1 , for pentane (1) + ethanol (3) at 303.15 K. The points are experimental results, the solid curve is the fitted P - x result, and the dashed curve is the predicted P - y result.

The resulting expression for the activity coefficient of species i is

$$\ln \gamma_i = \frac{\sum_j \tau_{ij} G_{ij} x_j}{\sum_j G_{ij} x_j} + \sum_l \frac{x_l G_{il}}{\sum_m G_{ml} x_m} \left(\tau_{il} - \frac{\sum_k \tau_{kl} G_{kl} x_k}{\sum_j G_{ij} x_j} + \frac{[\sum_k \tau_{kl} G_{kl} x_k][\sum_h G_{hl}^2 a_{ihl} x_h]}{[\sum_j G_{ij} x_j] G_{il}} - \frac{\sum_k \tau_{kl} G_{kl}^2 a_{kll} x_k}{G_{il}} \right) \quad (4)$$

With the additional assumptions that

$$\tau_{ij} = 0 \quad i = j \quad (5)$$

and

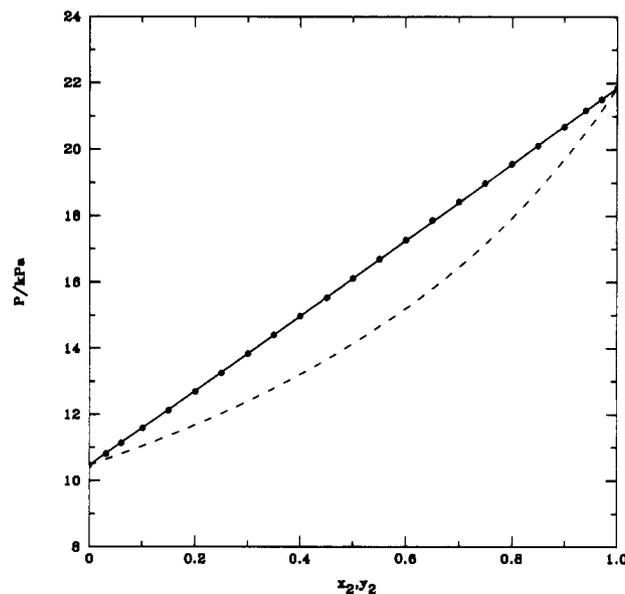
$$a_{kij} = 1.0 \quad i = j \quad (6)$$

eq 4 contains six adjustable values of τ_{ij} and eighteen adjustable values of a_{kij} for a ternary system. All of the τ_{ij} parameters and twelve of the a_{kij} parameters may be found from data for the constituent binary systems (each binary system is described by two values of τ_{ij} and four values of a_{kij}). Not all binary systems require six parameters to provide an adequate fit to the data, and special cases described by Campbell (9) may be applied in such instances.

Six of the a_{kij} parameters (those for which no two subscripts are the same) are ternary constants and require ternary data for their evaluation. Equation 4 has been found (9) to provide an excellent fit to data for systems consisting of two alcohols and a hydrocarbon and contains four fewer ternary parameters than the function used in previous studies (1, 2).

Table II. Total Pressure P as a Function of Liquid-Phase Mole Fraction x_i for Pentane (1) + Ethanol (3) and Methanol (2) + Ethanol (3) at 303.15 K

pentane (1) + ethanol (3)		methanol (2) + ethanol (3)	
x_1	P/kPa	x_2	P/kPa
0.0000	10.51	0.0000	10.47
0.0337	30.33	0.0325	10.81
0.0529	38.89	0.0611	11.13
0.0792	48.24	0.1017	11.59
0.1047	55.33	0.1500	12.12
0.1429	63.33	0.2005	12.69
0.1931	70.45	0.2501	13.25
0.2446	75.25	0.3003	13.83
0.2958	78.47	0.3499	14.40
0.3467	80.66	0.3997	14.97
0.3956	82.11	0.4504	15.53
0.3974	82.19	0.5000	16.11
0.4458	83.18	0.5497	16.69
0.4481	83.30	0.5999	17.27
0.4956	83.98	0.6492	17.85
0.4983	84.13	0.6500	17.87
0.5378	84.51	0.7001	18.43
0.5413	84.61	0.7496	18.99
0.6263	85.37	0.8005	19.57
0.6967	85.87	0.8503	20.11
0.7686	86.31	0.9002	20.68
0.8387	86.71	0.9402	21.17
0.9006	87.02	0.9706	21.50
0.9392	87.06	1.0000	21.85
0.9748	86.46		
1.0000	81.97		

**Figure 2.** Pressure P vs liquid-phase mole fraction x_2 , or vapor-phase mole fraction y_2 , for methanol (2) + ethanol (3) at 303.15 K. The points are experimental results, the solid curve is the fitted P - x result, and the dashed curve is the predicted P - y result.

Second molar virial coefficients and saturated liquid molar volumes at 303.15 K are required in the reduction of the data. Values used in the present study are shown in Table I. Saturated liquid volumes were taken from the same sources used for the room-temperature values. Second virial coefficients were calculated using the method of Tsonopoulos (11).

Results

Total pressure as a function of liquid-phase composition is reported for pentane + ethanol and methanol + ethanol at 303.15 K in Table II. P - x - y curves are shown in Figures 1 and 2. Binary parameters for these two systems are given in

Table III. Constants τ_{ij} and a_{kij} in Equation 4 for Pentane (1) + Ethanol (3) and Methanol (2) + Ethanol (3) at 303.15 K, Average Deviations ΔP_{av} , and Maximum Deviations ΔP_{max}

i,j	τ_{ij}	k,i,j	a_{kij}^a
1,3	1.880 17	1,1,3	13.959 44
3,1	1.836 78	3,1,3	5.289 43
2,3	-0.106 56	1,3,1	0.854 81
3,2	0.102 19	3,3,1	1.191 38
		2,2,3	0.963 39*
		3,2,3	0.963 39*
		2,3,2	1.034 61*
		3,3,2	1.034 61*
$\Delta P_{av\ 1,3}/\text{kPa} = 0.01$		$\Delta P_{max\ 1,3}/\text{kPa} = 0.06$	
$\Delta P_{av\ 2,3}/\text{kPa} = 0.02$		$\Delta P_{max\ 2,3}/\text{kPa} = 0.04$	

^a Values marked with an asterisk were calculated from eq 7, or its analogue, with $\alpha_{12} = 0.35$.

Table III, along with the corresponding average and maximum deviations in pressure.

For the pentane + ethanol system, all six binary parameters in eq 4 were treated as adjustable. No other data over the full range of composition could be located for this system at this temperature, so no comparison with previous results can be made. However, Cori and Delogu (12) measured infinite dilution activity coefficients for mixtures of ethanol and *n*-pentane and correlated their results with temperature. Infinite dilution activity coefficients predicted from the parameters in Table III are 9.61 for *n*-pentane and 56.0 for ethanol and are in fair and excellent agreement, respectively, with those calculated from the correlations of Cori and Delogu (8.96 and 56.2, respectively).

The full flexibility of eq 4 was not required to fit the nearly ideal methanol + ethanol system, and the number of parameters was reduced by making several assumptions. First, it was assumed that $a_{223} = a_{323}$ and $a_{232} = a_{332}$. Next it was assumed that

$$1/a_{223} = 1/a_{323} = G_{23} = \exp(-\alpha_{23}\tau_{23}) \quad (7)$$

with an analogous expression for a_{232} and a_{332} in terms of τ_{32} . Finally, it was assumed that $\alpha_{23} = \alpha_{32} = 0.35$. The resulting equation is the two-parameter form of the NRTL equation for which the resulting parameter values are given in Table III. Only values of τ_{23} and τ_{32} were obtained by regression; the a_{kij} values were calculated from eq 7 and its analogue.

Table IV. Total Pressure P for Pentane (1) + Methanol (2) + Ethanol (3) at 303.15 K as a Function of Liquid Mole Fractions x_1 and x_2 for Given Values of the Parameter C' , Equation 1

$C' = 0.2627$			$C' = 0.5061$			$C' = 0.7584$		
x_1	x_2	P/kPa	x_1	x_2	P/kPa	x_1	x_2	P/kPa
0.0279	0.2549	32.61	0.0271	0.4920	37.78	0.0269	0.7377	44.85
0.0557	0.2477	46.33	0.0551	0.4778	53.06	0.0646	0.7091	66.07
0.0940	0.2376	59.46	0.0943	0.4580	66.87	0.1040	0.6792	78.22
0.1439	0.2245	70.18	0.1441	0.4328	77.07	0.1439	0.6490	85.15
0.1941	0.2114	76.77	0.1945	0.4073	83.01	0.1946	0.6106	90.01
0.2446	0.1981	80.94	0.2450	0.3818	86.49	0.2451	0.5723	92.58
0.2956	0.1847	83.66	0.2958	0.3561	88.63	0.2535	0.5660	92.74
0.3463	0.1715	85.45	0.2957	0.3562	88.53	0.2954	0.5341	93.89
0.3464	0.1714	85.49	0.3454	0.3309	89.86	0.3450	0.4965	94.69
0.3963	0.1583	86.69	0.3949	0.3059	90.71	0.3946	0.4588	95.19
0.4461	0.1452	87.54	0.4447	0.2806	91.34	0.4450	0.4206	95.57
0.4966	0.1319	88.15	0.4953	0.2550	91.78	0.4950	0.3826	95.78
0.5458	0.1189	88.65	0.5448	0.2298	92.11	0.5451	0.3446	95.97
0.5962	0.1057	89.01	0.5959	0.2039	92.38	0.5957	0.3062	96.14
0.6467	0.0923	89.31	0.6460	0.1785	92.61	0.6458	0.2681	96.27
0.6972	0.0791	89.59	0.6972	0.1525	92.82	0.6973	0.2290	96.38
0.7475	0.0658	89.83	0.7481	0.1267	92.99	0.7481	0.1905	96.47
0.7986	0.0523	90.07	0.7983	0.1012	93.19	0.7990	0.1518	96.57
0.8516	0.0384	90.18	0.8501	0.0749	93.29	0.8499	0.1131	96.59
0.9000	0.0257	90.29	0.9022	0.0486	93.22	0.9022	0.0735	96.42
0.9407	0.0150	90.11	0.9417	0.0286	92.78	0.9436	0.0421	95.75
0.9759	0.0059	88.94	0.9764	0.0112	91.17	0.9736	0.0194	94.13

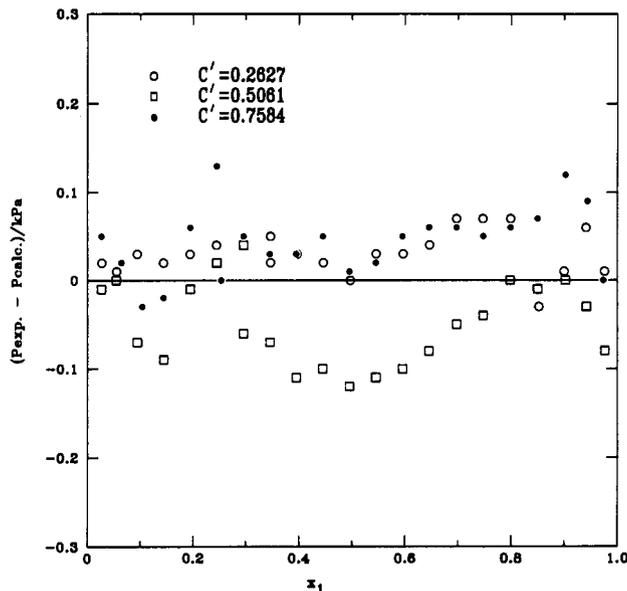


Figure 3. Pressure residuals $P_{exp} - P_{calc}$ for the ternary system pentane (1) + methanol (2) + ethanol (3) at 303.15 K (C' from eq 1).

Data for the methanol + ethanol system at 303.15 K were reported recently by Zielkiewicz et al. (13). After corrections are made for slight discrepancies (<0.02 kPa) in the pure component vapor pressures between studies, the two data sets agree to within an average of 0.01 kPa and the maximum discrepancy is 0.03 kPa.

Experimental P - x data for the ternary system are presented in Table IV. To regress the ternary measurements, it was necessary to choose average values for the pure component vapor pressures. Values of 82.03, 21.86, and 10.49 kPa were used for *n*-pentane, methanol, and ethanol, respectively. Since these values are slightly different from those reported in Table II, the pentane + ethanol and methanol + ethanol binary data were regressed again using the averaged vapor pressures. Furthermore, data reported earlier (2) for pentane + methanol were regressed using eq 4 and the average vapor pressures. The full six-parameter binary form of eq 4 was used for pentane + methanol and pentane + ethanol, while the two-constant

Table V. Constants in Equation 4 for the Ternary System Pentane (1) + Methanol (2) + Ethanol (3) at 303.15 K, Average Deviation ΔP_{av} , and Maximum Deviation ΔP_{max}

i,j	τ_{ij}	$k_{i,j}$	a_{kij}
1,2	1.973 54	1,1,2	16.759 36
2,1	2.438 85	2,1,2	3.590 74
1,3	1.857 32	1,2,1	0.968 88
3,1	1.832 95	2,2,1	1.576 15
2,3	0.002 03	1,1,3	13.748 54
3,2	-0.014 71	3,1,3	5.160 94
		1,3,1	0.854 58
		3,3,1	1.188 35
		2,2,3	1.000 72
		3,2,3	1.000 72
		2,3,2	0.994 87
		3,3,2	0.994 87
		1,2,3	0.623 48
		2,1,3	3.848 09
		1,3,2	1.818 05
		3,1,2	6.545 97
		2,3,1	1.298 04
		3,2,1	1.553 44

$$\Delta P_{av}/\text{kPa} = 0.05 \quad \Delta P_{max}/\text{kPa} = 0.13$$

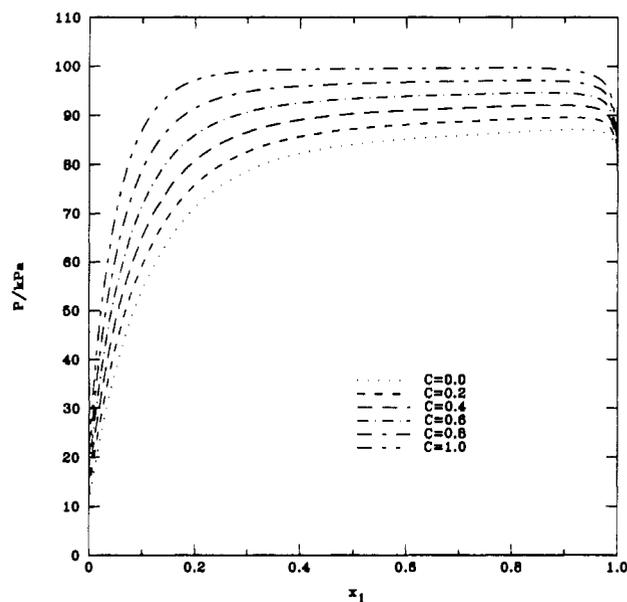


Figure 4. Pressure P vs mole fraction x_1 for pentane (1) + methanol (2) + ethanol (3) at 303.15 K (C from eq 8).

form was used for methanol + ethanol. All of the binary parameters are reported in Table V. It is worth noting that eq 4 provided a fit superior to that of the modified Margules equation for pentane + methanol (average deviation of 0.02 kPa compared to 0.11 kPa).

The last six values in the rightmost column of Table V represent the ternary parameters appearing in eq 4 and were obtained by regression of the ternary data using Barker's method. The average deviation between calculated and measured pressures for the ternary system was 0.05 kPa with a maximum deviation of 0.13 kPa. A plot of the pressure residuals is shown in Figure 3. The systematic discrepancy between one run (C'

= 0.5061) and the other two is within the experimental uncertainties quoted earlier.

P - x curves calculated using the parameter values given in Table V are shown in Figure 4. The parameter C , which appears in this figure, is defined by

$$C = \frac{x_2}{x_2 + x_3} \quad (8)$$

where x_2 and x_3 are the liquid-phase mole fractions of methanol and ethanol, respectively.

Glossary

a_{kij}	parameters for G^E , eq 3
B_{ij}	molar second virial coefficient for species i and j
C	ternary composition parameter, eq 8
C'	ternary composition parameter, eq 1
G_{ij}^E	composition-dependent function, eq 2
G^E	molar excess Gibbs energy
P	pressure
P_{calc}	calculated total pressure
P_{expt}	measured total pressure
ΔP_{av}	$(1/n) \sum_{i=1}^n P_{expt,i} - P_{calc,i} $
ΔP_{max}	$\max P_{expt,i} - P_{calc,i} $
R	universal gas constant
T	temperature
V_i^L	saturated molar volume of pure liquid i
x_i	liquid-phase mole fraction of species i
z_i	overall mole fraction of species i in equilibrium cell

Greek Letters

τ_{ij}	parameters for G^E , eq 2
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Registry No. Ethanol, 64-17-5; methanol, 67-56-1; pentane, 109-66-0.

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