Precision Total Pressure Measurements of Propyne with Propane, Propene, and Propadiene

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Experimental total pressure measurements of propyne mixed with propane, propene, and propadiene are presented for five isotherms from 253 to 353 K. Thermodynamically consistent vapor compositions and saturated phase densities are calculated using a cubic equation of state with three isothermal pure component parameters and two binary mixture parameters. The precision vapor–liquid equilibrium cell and experimental procedure which are particularly useful for measurements involving close boiling light hydrocarbons are described, and the experimental and modeled results are presented.

Introduction

The vapor–liquid equilibrium (VLE) behavior of acetylenic compounds in light hydrocarbon systems is poorly understood, with few data existing in the open literature. This class of compounds is known to commonly occur in petrochemical process streams as byproducts in many chemical processes. However, the reactions of acetylenic compounds and consequently the hazards posed by the presence of these compounds are well documented. Lacking accurate experimental data, it is difficult to predict how these compounds will behave in separation processes. Acetylenic compounds could be recovered as a product, but it is common practice to partially hydrogenate process streams in order to remove acetylenic compounds. Since the desired products in those streams are usually olefins or diolefins, a portion of the product is then lost in the process of eliminating the acetylenes. Decisions have to be made as to where and how much to hydrogenate. Accurate VLE predictions provide the ability to make more rational decisions in the design of separation processes.

Previous work with C3 hydrocarbons makes propyne a good choice for study. Higher molecular weight acetylenes are increasingly less stable, posing considerable safety risks. Accurate measurements of the acetylenic interactions in the C3 hydrocarbon system may prove useful to predict the VLE behavior of higher molecular weight acetylenes without incurring the safety risks associated with those compounds.

Experimental Section

Safety. Propyne and propadiene pose special safety problems beyond being flammable. Due to their unsaturated nature, both compounds are quite reactive. Propyne, as a primary alkyne, reacts with a number of metals including copper, silver, and mercury to form explosive metal acetylides. Both propyne and propadiene can undergo an explosive decomposition under pressures of 2–5 atm even in the absence of air. Higher molecular weight alkynes are far more unstable than propyne.

A number of references in the literature indicated possible hazard with use of acetylinic compounds with copper, silver, and mercury. However, Van Hook (1967) safely took vapor pressure measurements of propyne in a mercury manometer system up to pressures of 1000 mmHg. Rutledge (1969) is a comprehensive reference on the chemistry of acetylene compounds, but does not make statements about reactions with metals.

The explosive decomposition of propadiene and propyne was another area of concern. Rutledge (1969) and NFPA (1975) both list a number of references citing this hazard. Among them are Bondar et al. (1965), Yoshimine et al. (1967), Huston et al. (1970), Kuchta et al. (1964) and Vidaurri (1975). These references cited the hazards as being the ability to propagate a flame in the absence of oxygen at pressures of 2–5 atm. Several studies investigated stabilization by mixing in propene, 2-methylpropane, and other compounds. The risk for decomposition is greatest when the components are in a pure form.

The following precautions were taken to limit the risks of handling these compounds: (1) All stocks of propadiene and propyne were stored in a refrigerator/freezer. (2) All stocks of propyne were stored in stainless steel cylinders with stainless steel valves and fittings. (3) The amount of copper and silver left exposed to propyne vapor in the measurement cell was minimized. (4) Transfers of material were performed at low temperature/low pressure. (5) Distillations were done at low temperatures that kept the pressure below 1 atm. (6) Small amounts (approximately 2 g or less) of material were placed in the measurement cells.

Apparatus and Procedure. The total pressure technique requires the measurement of the temperature and pressure of a sample cell of known total volume with a known overall composition. The loaded measurement cells were placed in a temperature-controlled bath that was controlled between 253 and 353 K during this study. Maximum temperature gradients in the bath were less than 0.01 K. Bath temperature was measured with a standard platinum resistance thermometer utilizing a Mueller bridge and null detector system. Cross comparison with another standard platinum resistance thermometer indicated that temperature measurements in this study were within 0.01 K of IPTS-68. The manifold pressure that balanced the diaphragm against the measurement cell pressure was measured using a digital quartz pressure

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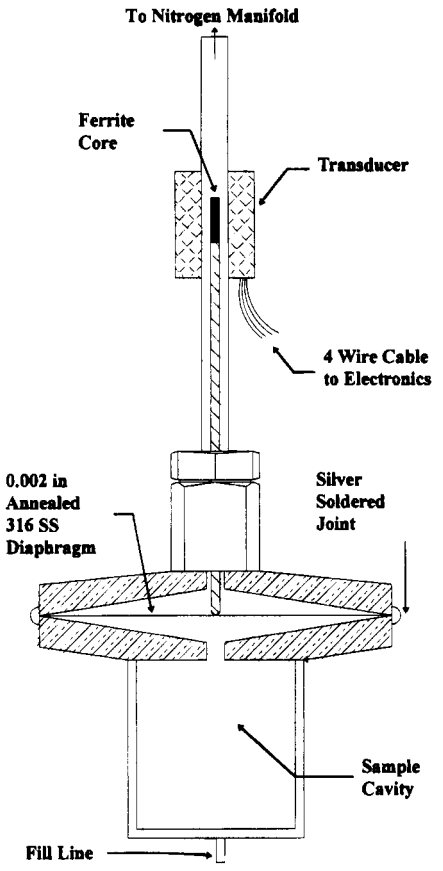

Figure 1. Total pressure measurement cell and transducer assembly.

gauge or a Ruska dead weight gauge. Ruska states the accuracy to be 0.04%. Pure component vapor pressure data were compared with literature values for propane, propene, and propyne and found to be within ±0.2% of what appeared to be reliable literature values.

The equipment and techniques developed to measure mixture vapor pressures drew heavily on past experiences with similar cells described by Barclay (1980), Flebbe (1980), and Burcham (1981). A welded cell design similar to that of Barclay was chosen to avoid problems with mechanical seals at the pressures of this study. Diaphragms were made from 316 and 316L annealed stainless steel diaphragm material ranging in thickness from 0.0010 to 0.0020 in. The measurement cell diameter was increased to 2.5 in. to increase the sensitivity of the cell. This caused additional difficulty in soldering the diaphragm between the halves of the measurement cell to seal the cell without damaging the diaphragm sensitivity to small pressure differentials. A total cavity depth of 0.035 in. was used. The pressure differential across the diaphragm was measured by sensing the position of the diaphragm with a pushrod/ferrite core assembly in the magnetic field of a transducer (above the temperature bath). The position of the diaphragm in each measurement cell was calibrated as a function of the pressure drop across the diaphragm and the null point determined as a percent of total diaphragm travel as the cell was under- and overpressurized. Pressure and temperature effects on the null point were small. The overall accuracy of measuring pressure using the Ruska gauge and these cells was estimated to be 0.1%.

Cell volumes ranged from 6.13 to 7.65 cm^3. Each cell volume was determined by loading distilled water into an evacuated cell. The diaphragm cavity was estimated to be on the order of 0.3 cm^3. On the basis of duplicate measurements the uncertainty in the cell volume was estimated to be 0.01 cm^3 or less than 0.2%.

Evacuated measurement cells were loaded from 10% to 60% full of liquid hydrocarbon via a manifold and hand pump with purified degassed liquid phase components. The least volatile component was loaded first, and the mass of each component loaded into each cell was determined by the mass difference as determined on a large capacity beam balance with a sensitivity of 0.1 mg. A series of six cells was loaded and placed in the temperature bath. Each cell was attached to a nitrogen gas manifold where the pressure was adjusted with a hand pump and measured with the Ruska dead weight gauge or digital quartz pressure gauge previously described. The system was equilibrated, and measurements were taken for each cell. Five isotherms were measured in duplicate with each set of cells. The temperature was cycled such that the low temperatures were measured both at the start and at the end of the series in order to detect any chemical changes in the contents of the cells at the high temperatures.

Source Chemicals and Purification. Propane and propene in purities of 99.99% were available for this study. Propadiene (96% purity) from Burcham's work (1981, 1986) was available. Additional propadiene and propyne were obtained in purities of 96%. Purification of the propadiene and propyne was accomplished by performing batch distillations in a jacketed 1.52 m silvered distillation column filled with 6 mm Raschig rings at or slightly below atmospheric pressure. Composition was determined by a flame ionization detector (FID) gas chromatograph (GC) analysis of liquid phase samples. High purity propyne was prepared; however, the separation of butane from propadiene seemed to be limited by the apparatus. Successive batch distillations were unable to achieve a significant increase in purity. Pressurized distillation may have eliminated this problem, but would have entailed safety risks.

Positive identification of the impurity peaks from the gas chromatagraph was accomplished by spiking samples with butane and 2-methylpropane and observing the unknown impurity peak that increased. Propane and propene retention times were determined directly. This identification process contradicted the results for the impurities in propadiene reported by Burcham (1981, 1986).

All chemicals were degassed to remove noncondensable gases by freezing in liquid nitrogen and evacuating the vapor space in the sample cylinder. Seven to ten freeze–evacuate–thaw cycles were performed on each sample. Both vapor and liquid phase samples were analyzed by a gas chromatograph with a thermal conductivity detector (TCD) to detect air. These analyses indicated that the maximum air content of a liquid phase sample from any of the chemicals was less than 0.02 mol %. All loading of cells was performed from the liquid phase of the sample cylinder.

The final mole fraction purity of each of the purified chemicals is listed in Table 1. The propane and propene purities were determined by lot analyses by the manufacturer, and the propadiene and propyne purities were determined by GC/FID after distillation.

Liquid phase samples from loaded measurement cells of each pure component were analyzed by GC/TCD after being subjected to the full range of temperatures and pressures of the measurement. No evidence of significant air introduction during the loading process nor decomposition during the measurement process was observed.

Table 1. Mole Fraction Purity of Raw Chemicals after Purification

	propane	propene	propadiene	propyne	butane	2-methylpropane	ethane
propane	0.999 9						0.0001
propene	0.000 1	0.999 9					
propadiene	0.000 07	0.000 25	0.964 85	0.003 81	0.031 00	0.000 01	
propyne	0.000 00	0.000 00	0.000 16	0.999 76	0.000 08		

Table 2. Temperature-Adjusted Results for Propane + Propyne with Values for Liquid Mole Fractions[a]

T/K	*P*/kPa			propane	propadiene	propyne	butane
253.15	115.45	115.49	115.61		0.000 16	0.999 76	0.000 08
	115.63				0.000 16	0.999 76	0.000 08
278.15	302.16	302.27	302.46		0.000 16	0.999 76	0.000 08
	302.62	303.27			0.000 16	0.999 76	0.000 08
303.15	663.31	663.62	663.89		0.000 16	0.999 76	0.000 08
	664.27				0.000 16	0.999 76	0.000 08
328.15	1279.07	1279.38	1279.49		0.000 16	0.999 76	0.000 08
353.15	2239.27	2239.70	2240.05		0.000 16	0.999 76	0.000 08
	2240.21				0.000 16	0.999 76	0.000 08
253.15	163.41	164.43		0.108 56	0.000 14	0.891 23	0.000 07
278.15	388.98	389.30	390.42	0.108 12	0.000 14	0.891 67	0.000 07
303.15	801.17	802.27		0.107 72	0.000 14	0.892 07	0.000 07
328.15	1479.08	1480.95		0.107 48	0.000 14	0.892 31	0.000 07
353.15	2517.49	2518.41		0.107 60	0.000 14	0.892 19	0.000 07
253.15	208.14	208.34		0.295 72	0.000 11	0.704 11	0.000 05
278.15	476.01	477.02	477.32	0.292 58	0.000 11	0.707 26	0.000 05
303.15	949.36	949.57		0.288 83	0.000 11	0.711 00	0.000 05
328.15	1705.80	1706.30		0.284 88	0.000 11	0.714 95	0.000 06
353.15	2837.57	2839.29		0.281 24	0.000 11	0.718 59	0.000 06
253.15	218.81	218.84		0.366 61	0.000 10	0.633 24	0.000 05
278.15	497.66	497.96		0.361 38	0.000 10	0.638 47	0.000 05
303.15	987.08	987.81		0.354 86	0.000 10	0.644 98	0.000 05
328.15	1765.66	1765.70		0.347 61	0.000 10	0.652 24	0.000 05
353.15	2923.34	2924.40		0.340 09	0.000 10	0.659 75	0.000 06
253.15	228.15	228.18		0.451 59	0.000 09	0.548 28	0.000 04
278.15	518.89	519.85	519.95	0.450 32	0.000 09	0.549 55	0.000 04
303.15	1027.54	1027.86		0.448 89	0.000 09	0.550 98	0.000 04
328.15	1834.30	1834.94		0.447 60	0.000 09	0.552 27	0.000 04
353.15	3035.75	3038.91		0.447 08	0.000 09	0.552 79	0.000 04
253.15	229.88	230.00		0.466 29	0.000 09	0.533 58	0.000 04
278.15	521.57	522.26	523.64	0.465 15	0.000 09	0.534 72	0.000 04
	524.01						
303.15	1033.50	1035.01		0.463 87	0.000 09	0.536 00	0.000 04
328.15	1844.06	1845.65		0.462 76	0.000 09	0.537 11	0.000 04
353.15	3046.54	3050.71		0.462 43	0.000 09	0.537 44	0.000 04
253.15	242.79	243.43		0.629 48	0.000 06	0.370 43	0.000 03
278.15	550.77	552.20		0.628 66	0.000 06	0.371 25	0.000 03
303.15	1086.96	1087.05	1087.21	0.627 78	0.000 06	0.372 13	0.000 03
328.15	1933.20	1933.36		0.627 08	0.000 06	0.372 83	0.000 03
353.15	3188.27	3188.85		0.626 90	0.000 06	0.373 01	0.000 03
253.15	244.43	245.74		0.644 33	0.000 06	0.355 59	0.000 03
278.15	553.52	553.58	555.74	0.642 65	0.000 06	0.357 27	0.000 03
303.15	1091.90	1092.49	1092.92	0.640 73	0.000 06	0.359 18	0.000 03
328.15	1940.00	1940.11		0.638 96	0.000 06	0.360 95	0.000 03
353.15	3197.56	3198.41		0.637 59	0.000 06	0.362 31	0.000 03
253.15	246.27	246.47		0.683 75	0.000 05	0.316 18	0.000 02
278.15	557.79	558.23		0.683 15	0.000 05	0.316 78	0.000 02
303.15	1098.16	1098.31		0.682 56	0.000 05	0.317 37	0.000 02
328.15	1949.99	1950.62		0.682 17	0.000 05	0.317 75	0.000 03
353.15	3213.96	3214.15		0.682 19	0.000 05	0.317 74	0.000 03
253.15	248.56	248.63		0.739 84	0.000 04	0.260 10	0.000 02
278.15	562.81	562.87		0.739 43	0.000 04	0.260 51	0.000 02
303.15	1105.93	1106.11		0.739 11	0.000 04	0.260 83	0.000 02
328.15	1960.82	1961.06		0.739 04	0.000 04	0.260 90	0.000 02
353.15	3227.26	3227.34		0.739 29	0.000 04	0.260 65	0.000 02
253.15	244.85	244.93		1.000 00	0.000 00	0.000 00	0.000 00
278.15	550.95	551.73	552.70	1.000 00			
303.15	1080.38	1081.51		1.000 00			
328.15	1909.12	1909.55		1.000 00			
353.15	3133.05	3133.05		1.000 00			

[a] Multiple pressures result from independent *T*, *P* equilibrations with the same loaded cells adjusted to the target temperature.

Data Reduction. Total pressure measurements from each cell were adjusted from the experimental temperature to the target value of temperature using a Wagner equation fit (Ambrose, 1986) of five isotherms measured in this study. Deviations between the experimentally determined pressure and the value predicted by the equation at the experimental temperatures were added to the pressure predicted from the equation at the target temperature. This kept any lack of fit of the equation from affecting the corrected values of pressure. One temperature adjustment

Table 3. Temperature-Adjusted Results for Propene + Propyne with Values for Liquid Mole Fractions[a]

T/K	P/kPa		propane	propene	propadiene	propyne	butane
253.15	115.45	115.49	0.000 00		0.000 16	0.999 76	0.000 08
	115.61	115.63	0.000 00		0.000 16	0.999 76	0.000 08
278.15	302.16	302.27	0.000 00		0.000 16	0.999 76	0.000 08
	302.46	302.62	0.000 00		0.000 16	0.999 76	0.000 08
	303.27		0.000 00		0.000 16	0.999 76	0.000 08
303.15	663.31	663.62	0.000 00		0.000 16	0.999 76	0.000 08
	663.89	664.27	0.000 00		0.000 16	0.999 76	0.000 08
328.15	1279.07	1279.38	0.000 00		0.000 16	0.999 76	0.000 08
	1279.49		0.000 00		0.000 16	0.999 76	0.000 08
353.15	2239.27	2239.70	0.000 00		0.000 16	0.999 76	0.000 08
	2240.05	2240.21	0.000 00		0.000 16	0.999 76	0.000 08
253.15	145.87	146.23	0.000 01	0.096 48	0.000 14	0.903 30	0.000 07
278.15	358.93	359.13	0.000 01	0.094 43	0.000 14	0.905 35	0.000 07
303.15	755.13	755.49	0.000 01	0.092 03	0.000 14	0.907 75	0.000 07
328.15	1413.70	1414.22	0.000 01	0.089 50	0.000 14	0.910 28	0.000 07
353.15	2425.14	2425.55	0.000 01	0.087 05	0.000 14	0.912 73	0.000 07
253.15	201.75	202.32	0.000 03	0.311 06	0.000 11	0.688 74	0.000 05
278.15	467.46	467.79	0.000 03	0.306 65	0.000 11	0.693 15	0.000 05
303.15	938.19	938.82	0.000 03	0.301 23	0.000 11	0.698 58	0.000 05
328.15	1693.39	1694.83	0.000 03	0.295 16	0.000 11	0.704 64	0.000 05
353.15	2824.11	2825.03	0.000 03	0.288 89	0.000 11	0.710 92	0.000 06
253.15	235.99	237.62	0.000 05	0.491 39	0.000 08	0.508 44	0.000 04
278.15	536.67	537.85	0.000 05	0.487 82	0.000 08	0.512 01	0.000 04
303.15	1060.79	1061.00	0.000 05	0.483 39	0.000 08	0.516 44	0.000 04
328.15	1889.78	1890.83	0.000 05	0.478 40	0.000 08	0.521 43	0.000 04
353.15	3121.90	3128.37	0.000 05	0.473 36	0.000 08	0.526 47	0.000 04
253.15	267.45	267.73	0.000 07	0.697 88	0.000 05	0.301 98	0.000 02
278.15	600.85	601.16	0.000 07	0.696 78	0.000 05	0.303 08	0.000 02
303.15	1175.58	1176.05	0.000 07	0.695 53	0.000 05	0.304 33	0.000 02
328.15	2078.72	2079.41	0.000 07	0.694 36	0.000 05	0.305 50	0.000 02
353.15	3414.04	3414.46	0.000 07	0.693 95	0.000 05	0.305 91	0.000 02
253.15	294.79	295.30	0.000 09	0.900 01	0.000 02	0.099 88	0.000 01
278.15	655.17	655.60	0.000 09	0.898 90	0.000 02	0.100 98	0.000 01
303.15	1269.50	1270.32	0.000 09	0.897 53	0.000 02	0.102 35	0.000 01
328.15	2227.42	2228.17	0.000 09	0.896 00	0.000 02	0.103 89	0.000 01
353.15	3637.62	3638.03	0.000 09	0.894 71	0.000 02	0.105 18	0.000 01
253.15	305.95	306.00	0.000 10	0.999 90			
	305.96		0.000 10	0.999 90			
278.15	676.57	676.65	0.000 10	0.999 90			
303.15	1305.71	1306.19	0.000 10	0.999 90			
328.15	2283.22	2283.40	0.000 10	0.999 90			
	2282.69		0.000 10	0.999 90			
353.15	3710.01	3716.45	0.000 10	0.999 90			

[a] Multiple pressures result from independent T, P, equilibrations with the same loaded cells adjusted to the target temperature.

was 1.02 K, with the rest less than 0.2 K and most less than 0.03 K. These adjustments resulted in pressure adjustments of less than 0.4% and typically less than 0.1% except for the one value that was adjusted 3.5–4%. The error introduced into the results by this adjustment was not generally significant.

Measurement of temperature T, pressure P, moles of each component loaded, and cell volume V^{cell} completely determines the system. Therefore, an appropriate thermodynamic model can be applied along with equilibrium constraints and a material balance to solve for all the other variables. This allows the experimental results to be converted into T, P, x_i, and y_i results for each data point. VLE behavior throughout the composition range can also be predicted within the ability of the thermodynamic model chosen. In this study the Peneloux equation of state (EOS) (Peneloux et al., 1982) with mixing rules as suggested by Panagiotopoulos and Reid (1986) was used (eqs 1–4). A flash calculation (eq 5) and a material balance for each component (eq 6) completed the specification of the system.

$$P = \frac{RT}{V-b} - \frac{a}{(V+c)(V+b+2c)} \tag{1}$$

where a, b, and c are pure component EOS parameters, V is the molar volume, and R is the ideal gas constant.

The Panagiotopoulos modifications of the mixing rules are

$$a = \sum_i \sum_j x_i x_j ((a_i a_j)^{1/2}(1 - k_{ij}) + (2b/VRT)x_i \lambda_{ij}) \tag{2}$$

$$k_{ij} = k_{ji} \quad \lambda_{ij} = -\lambda_{ji}$$

$$b = \sum_i x_i b_i \tag{3}$$

$$c = \sum_i x_i c_i \tag{4}$$

$$l = \frac{V^v - V^{cell}/N^{cell}}{V^v - V^l} \tag{5}$$

$$x_i = \frac{z_i}{l - K_i(1-l)} \tag{6}$$

where k_{ij} and λ_{ij} are EOS binary mixture parameters, l is the fraction of total moles in the liquid phase, N is moles,

Table 4. Temperature-Adjusted Results for Propadiene + Propyne with Values for Liquid Mole Fractions[a]

T/K	P/kPa		propane	propene	propadiene	propyne	butane	2-methylpropane
253.15	115.45	115.49	0.000 00		0.000 16	0.999 76	0.000 08	
	115.61	115.63	0.000 00		0.000 16	0.999 76	0.000 08	
278.15	302.16	302.27	0.000 00		0.000 16	0.999 76	0.000 08	
	302.46	302.62	0.000 00		0.000 16	0.999 76	0.000 08	
	303.27		0.000 00		0.000 16	0.999 76	0.000 08	
303.15	663.31	663.62	0.000 00		0.000 16	0.999 76	0.000 08	
	663.89	664.27	0.000 00		0.000 16	0.999 76	0.000 08	
328.15	1279.07	1279.38	0.000 00		0.000 16	0.999 76	0.000 08	
	1279.49		0.000 00		0.000 16	0.999 76	0.000 08	
353.15	2239.27	2239.70	0.000 00		0.000 16	0.999 76	0.000 08	
	2240.05	2240.21	0.000 00		0.000 16	0.999 76	0.000 08	
253.15	125.13	125.13	0.000 01	0.000 02	0.096 19	0.900 60	0.003 18	0.000 00
278.15	321.43	321.56	0.000 01	0.000 02	0.095 53	0.901 27	0.003 17	0.000 00
303.15	695.83	695.92	0.000 01	0.000 02	0.094 73	0.902 08	0.003 16	0.000 00
328.15	1328.99	1329.03	0.000 01	0.000 02	0.093 81	0.902 99	0.003 16	0.000 00
353.15	2310.46	2310.53	0.000 01	0.000 02	0.092 86	0.903 92	0.003 19	0.000 00
253.15	141.64	141.80	0.000 02	0.000 07	0.279 19	0.711 64	0.009 08	0.000 00
278.15	354.55	354.66	0.000 02	0.000 07	0.278 26	0.712 56	0.009 08	0.000 00
303.15	752.94	753.00	0.000 02	0.000 07	0.277 13	0.713 67	0.009 10	0.000 00
328.15	1416.83	1416.96	0.000 02	0.000 07	0.275 93	0.714 82	0.009 16	0.000 00
353.15	2436.27	2436.31	0.000 02	0.000 07	0.274 87	0.715 79	0.009 26	0.000 00
253.15	155.68	155.69	0.000 03	0.000 12	0.462 69	0.522 18	0.014 97	0.000 01
278.15	382.62	382.70	0.000 03	0.000 12	0.462 07	0.522 77	0.014 99	0.000 01
303.15	801.38	801.45	0.000 03	0.000 12	0.461 35	0.523 45	0.015 05	0.000 01
328.15	1491.34	1491.59	0.000 03	0.000 12	0.460 64	0.524 07	0.015 14	0.000 01
353.15	2542.37	2542.53	0.000 03	0.000 12	0.460 13	0.524 45	0.015 26	0.000 01
253.15	167.91	167.92	0.000 05	0.000 17	0.658 58	0.319 80	0.021 39	0.000 01
278.15	406.62	406.71	0.000 05	0.000 17	0.657 56	0.320 68	0.021 53	0.000 01
303.15	842.13	842.28	0.000 05	0.000 17	0.656 28	0.321 70	0.021 79	0.000 01
328.15	1552.78	1552.80	0.000 05	0.000 16	0.654 87	0.322 69	0.022 22	0.000 01
353.15	2624.77	2627.16	0.000 05	0.000 16	0.653 40	0.323 56	0.022 83	0.000 01
253.15	179.26	179.42	0.000 06	0.000 23	0.864 88	0.106 90	0.027 91	0.000 01
278.15	428.14	428.20	0.000 06	0.000 23	0.864 69	0.107 00	0.028 01	0.000 01
303.15	877.03	877.37	0.000 06	0.000 23	0.864 43	0.107 10	0.028 17	0.000 01
328.15	1603.52	1603.90	0.000 06	0.000 22	0.864 12	0.107 19	0.028 39	0.000 01
353.15	2693.29	2695.33	0.000 06	0.000 22	0.863 75	0.107 30	0.028 65	0.000 01
253.15	183.59	183.66	0.000 07	0.000 25	0.963 95	0.003 84	0.031 88	0.000 01
278.15	436.14	436.30	0.000 07	0.000 24	0.963 05	0.003 87	0.032 76	0.000 01
303.15	889.49	889.65	0.000 07	0.000 23	0.961 40	0.003 89	0.034 40	0.000 01
328.15	1620.14	1620.43	0.000 06	0.000 22	0.958 50	0.003 91	0.037 29	0.000 02
353.15	2714.53	2715.48	0.000 06	0.000 21	0.953 37	0.003 96	0.042 38	0.000 02

[a] Multiple pressures result from independent T, P equilibrations with the same loaded cells adjusted to the target temperature.

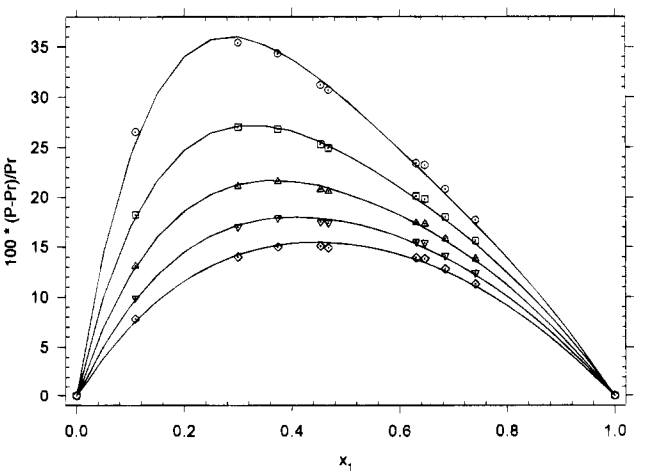

Figure 2. Comparison of the Raoult's law pressure deviations for experimental data and the model for propane (1) + propyne (2): dotted circle, 253.15 K; dotted square, 278.15 K; dotted triangle, 303.15 K; dotted inverted triangle, 328.15 K; dotted tilted square, 353.15 K.

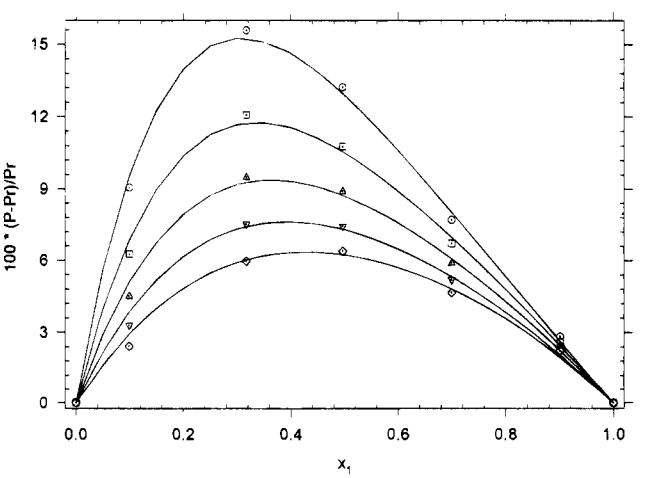

Figure 3. Comparison of the Raoult's law pressure deviations for experimental data and the model for propene (1) + propyne (2): dotted circle, 253.15 K; dotted square, 278.15 K; dotted triangle, 303.15 K; dotted inverted triangle, 328.15 K; dotted tilted square, 353.15 K.

the superscripts v, l and cell refer to the vapor phase, liquid phase, and the overall cell, respectively, z_i refers to the overall mole fraction for both phases combined, and $K_i = y_i/x_i$.

Pure component a_i, b_i, and c_i were fit at each isotherm to the best pure component physical property values of saturated vapor and liquid molar volumes available and the saturated pressure values of this study. Each set of

Table 5. Calculated Liquid and Vapor Mole Fractions x_1 and y_1, Pressure, Liquid Molar Volume V^l, Vapor Compressibility Z, and Relative Volatility α for Propane (1) + Propyne (2)

T/K	x_1	y_1	P/kPa	V^l/(cm³ mol⁻¹)	Z	α	T/K	x_1	y_1	P/kPa	V^l/(cm³ mol⁻¹)	Z	α
253.15	0.00	0.000	115.56	59.9	0.950	5.317	328.15	0.00	0.000	1279.18	71.4	0.813	2.283
253.15	0.05	0.204	139.62	61.4	0.946	4.856	328.15	0.05	0.102	1378.06	73.0	0.801	2.154
253.15	0.10	0.330	159.54	62.8	0.942	4.427	328.15	0.10	0.184	1464.93	74.8	0.789	2.033
253.15	0.15	0.416	176.02	64.2	0.938	4.029	328.15	0.15	0.253	1541.39	76.5	0.778	1.920
253.15	0.20	0.478	189.54	65.6	0.935	3.661	328.15	0.20	0.312	1608.75	78.3	0.768	1.814
253.15	0.25	0.526	200.71	66.8	0.933	3.322	328.15	0.25	0.364	1668.05	80.1	0.759	1.716
253.15	0.30	0.563	209.88	68.0	0.931	3.012	328.15	0.30	0.411	1720.38	81.9	0.751	1.625
253.15	0.35	0.595	217.46	69.2	0.929	2.727	328.15	0.35	0.453	1766.51	83.7	0.743	1.540
253.15	0.40	0.622	223.80	70.3	0.928	2.467	328.15	0.40	0.494	1807.05	85.5	0.736	1.462
253.15	0.45	0.646	229.18	71.3	0.927	2.230	328.15	0.45	0.532	1842.62	87.3	0.730	1.389
253.15	0.50	0.668	233.73	72.3	0.926	2.016	328.15	0.50	0.569	1873.51	89.0	0.724	1.321
253.15	0.55	0.690	237.66	73.2	0.925	1.821	328.15	0.55	0.606	1899.85	90.7	0.719	1.257
253.15	0.60	0.712	241.04	74.0	0.925	1.645	328.15	0.60	0.643	1921.84	92.3	0.715	1.199
253.15	0.65	0.734	243.94	74.8	0.924	1.487	328.15	0.65	0.680	1939.36	93.8	0.711	1.144
253.15	0.70	0.758	246.35	75.5	0.924	1.345	328.15	0.70	0.718	1952.18	95.2	0.708	1.093
253.15	0.75	0.785	248.21	76.3	0.925	1.219	328.15	0.75	0.758	1960.18	96.5	0.705	1.045
253.15	0.80	0.816	249.45	76.9	0.925	1.106	328.15	0.80	0.800	1962.87	97.6	0.704	0.999
253.15	0.85	0.851	250.00	77.6	0.926	1.006	328.15	0.85	0.844	1959.77	98.6	0.703	0.956
253.15	0.90	0.892	249.52	78.2	0.927	0.919	328.15	0.90	0.892	1950.32	99.4	0.703	0.916
253.15	0.95	0.941	247.94	78.8	0.928	0.843	328.15	0.95	0.943	1933.77	100.0	0.704	0.877
253.15	1.00	1.000	244.90	79.5	0.931	0.777	328.15	1.00	1.000	1909.37	100.5	0.706	0.839
278.15	0.00	0.000	302.54	63.0	0.917	3.881	353.15	0.00	0.000	2239.69	78.5	0.717	1.830
278.15	0.05	0.158	346.39	64.4	0.910	3.559	353.15	0.05	0.084	2373.59	80.6	0.701	1.744
278.15	0.10	0.266	383.00	65.9	0.904	3.266	353.15	0.10	0.156	2493.97	82.8	0.686	1.663
278.15	0.15	0.346	413.69	67.3	0.898	3.000	353.15	0.15	0.219	2602.15	85.1	0.672	1.587
278.15	0.20	0.408	439.47	68.7	0.893	2.757	353.15	0.20	0.275	2699.23	87.5	0.658	1.516
278.15	0.25	0.458	461.26	70.0	0.889	2.535	353.15	0.25	0.326	2786.31	90.0	0.645	1.450
278.15	0.30	0.500	479.74	71.4	0.885	2.333	353.15	0.30	0.373	2864.29	92.6	0.632	1.389
278.15	0.35	0.536	495.53	72.7	0.882	2.149	353.15	0.35	0.418	2933.99	95.3	0.620	1.332
278.15	0.40	0.569	509.11	73.9	0.879	1.981	353.15	0.40	0.461	2995.98	98.0	0.609	1.280
278.15	0.45	0.599	520.76	75.1	0.877	1.827	353.15	0.45	0.502	3050.59	100.7	0.599	1.232
278.15	0.50	0.628	530.97	76.2	0.875	1.687	353.15	0.50	0.543	3098.02	103.3	0.589	1.188
278.15	0.55	0.656	539.72	77.3	0.873	1.558	353.15	0.55	0.584	3138.29	105.9	0.581	1.148
278.15	0.60	0.684	547.17	78.4	0.872	1.440	353.15	0.60	0.625	3171.38	108.4	0.573	1.111
278.15	0.65	0.712	553.51	79.3	0.871	1.332	353.15	0.65	0.667	3196.96	110.7	0.566	1.077
278.15	0.70	0.742	558.54	80.3	0.870	1.233	353.15	0.70	0.709	3214.82	112.8	0.561	1.046
278.15	0.75	0.774	562.20	81.1	0.870	1.141	353.15	0.75	0.753	3224.40	114.6	0.556	1.017
278.15	0.80	0.809	564.40	81.9	0.870	1.057	353.15	0.80	0.798	3225.37	116.0	0.553	0.990
278.15	0.85	0.847	564.82	82.6	0.870	0.980	353.15	0.85	0.845	3217.23	117.1	0.552	0.964
278.15	0.90	0.891	563.16	83.3	0.871	0.909	353.15	0.90	0.894	3199.51	117.8	0.552	0.939
278.15	0.95	0.941	559.03	84.0	0.872	0.843	353.15	0.95	0.946	3171.66	118.2	0.553	0.915
278.15	1.00	1.000	551.79	84.6	0.874	0.783	353.15	1.00	1.000	3133.05	118.1	0.556	0.891
303.15	0.00	0.000	663.69	66.6	0.874	2.914							
303.15	0.05	0.125	732.43	68.1	0.864	2.712							
303.15	0.10	0.219	791.45	69.6	0.856	2.527							
303.15	0.15	0.294	842.13	71.1	0.848	2.356							
303.15	0.20	0.355	885.91	72.7	0.841	2.198							
303.15	0.25	0.406	923.69	74.2	0.834	2.053							
303.15	0.30	0.451	956.51	75.7	0.829	1.919							
303.15	0.35	0.492	985.05	77.1	0.824	1.796							
303.15	0.40	0.529	1009.94	78.6	0.820	1.681							
303.15	0.45	0.563	1031.66	80.0	0.816	1.576							
303.15	0.50	0.597	1050.49	81.4	0.812	1.478							
303.15	0.55	0.629	1066.69	82.7	0.809	1.388							
303.15	0.60	0.662	1080.34	84.0	0.807	1.304							
303.15	0.65	0.695	1091.58	85.1	0.805	1.226							
303.15	0.70	0.729	1100.20	86.2	0.803	1.153							
303.15	0.75	0.765	1106.06	87.3	0.802	1.086							
303.15	0.80	0.804	1108.95	88.2	0.801	1.022							
303.15	0.85	0.845	1108.47	89.1	0.801	0.963							
303.15	0.90	0.891	1104.06	89.8	0.802	0.907							
303.15	0.95	0.942	1095.16	90.5	0.803	0.854							
303.15	1.00	1.000	1080.96	91.1	0.805	0.804							

isothermal mixture data was then fit to two mixture constants, k_{ij} and λ_{ij}. Two mixture parameters were used because the fit of this data within experimental error could not be done with a single mixture parameter. The same values for pure and mixture parameters were used for both the liquid and vapor phases. Both the pure component parameters and the mixture parameters were regressed with a finite difference Levenberg–Marquardt algorithm to minimize the sum of the squares of the relative difference between the experimentally determined pressures and those predicted by the model and parameter values as shown in eq 7, where $k = 1$ to the total number of data

$$f(x) = \sum_k \frac{(P_{exp} - P_{model}(a_i,b_i,c_i,k_{i,j},\lambda_{i,j}))}{P_{exp}} \quad (7)$$

points for the isotherm. All isothermal data points for each binary mixture were regressed together. Due to the impurities present in the propadiene used for this study,

Table 6. Calculated Liquid and Vapor Mole Fractions x_1 and y_1, Pressure, Liquid Molar Volume V^l, Vapor Compressibility Z, and Relative Volatility α for Propene (1) + Propyne (2)

T/K	x_1	y_1	P/kPa	V^l/(cm^3 mol^{-1})	Z	α	T/K	x_1	y_1	P/kPa	V^l/(cm^3 mol^{-1})	Z	α
253.15	0.00	0.000	115.56	59.9	0.950	3.817	328.15	0.00	0.000	1279.18	71.4	0.813	1.986
253.15	0.05	0.162	132.10	60.8	0.947	3.680	328.15	0.05	0.092	1358.06	72.4	0.804	1.934
253.15	0.10	0.283	147.55	61.7	0.945	3.545	328.15	0.10	0.173	1432.87	73.5	0.795	1.882
253.15	0.15	0.376	161.82	62.6	0.943	3.410	328.15	0.15	0.244	1503.88	74.6	0.787	1.831
253.15	0.20	0.450	175.13	63.4	0.940	3.278	328.15	0.20	0.308	1571.32	75.7	0.779	1.781
253.15	0.25	0.512	187.54	64.2	0.938	3.147	328.15	0.25	0.366	1635.30	76.9	0.770	1.732
253.15	0.30	0.564	199.05	65.0	0.936	3.017	328.15	0.30	0.419	1696.11	78.0	0.763	1.684
253.15	0.35	0.609	209.74	65.8	0.934	2.890	328.15	0.35	0.468	1753.89	79.2	0.755	1.637
253.15	0.40	0.648	219.80	66.5	0.932	2.765	328.15	0.40	0.515	1808.84	80.5	0.747	1.591
253.15	0.45	0.684	229.18	67.2	0.931	2.642	328.15	0.45	0.559	1861.10	81.7	0.740	1.546
253.15	0.50	0.716	238.01	67.9	0.929	2.522	328.15	0.50	0.601	1910.95	83.0	0.733	1.503
253.15	0.55	0.746	246.28	68.5	0.928	2.404	328.15	0.55	0.641	1958.39	84.2	0.727	1.462
253.15	0.60	0.774	254.21	69.1	0.927	2.288	328.15	0.60	0.681	2003.62	85.5	0.720	1.421
253.15	0.65	0.802	261.66	69.7	0.925	2.175	328.15	0.65	0.720	2046.64	86.7	0.714	1.382
253.15	0.70	0.828	268.83	70.3	0.924	2.065	328.15	0.70	0.758	2087.53	87.9	0.708	1.345
253.15	0.75	0.855	275.65	70.8	0.923	1.958	328.15	0.75	0.797	2126.21	89.1	0.702	1.308
253.15	0.80	0.881	282.20	71.3	0.923	1.853	328.15	0.80	0.836	2162.61	90.3	0.697	1.274
253.15	0.85	0.909	288.55	71.7	0.922	1.752	328.15	0.85	0.875	2196.67	91.4	0.692	1.240
253.15	0.90	0.937	294.61	72.2	0.922	1.654	328.15	0.90	0.916	2228.25	92.5	0.687	1.208
253.15	0.95	0.967	300.47	72.6	0.921	1.559	328.15	0.95	0.957	2257.21	93.5	0.683	1.177
253.15	1.00	1.000	305.99	73.0	0.921	1.467	328.15	1.00	1.000	2283.13	94.4	0.679	1.147
278.15	0.00	0.000	302.54	63.0	0.917	2.956	353.15	0.00	0.000	2239.69	78.5	0.717	1.666
278.15	0.05	0.131	333.98	63.9	0.913	2.857	353.15	0.05	0.079	2350.70	79.8	0.706	1.628
278.15	0.10	0.235	363.35	64.8	0.909	2.760	353.15	0.10	0.150	2457.29	81.1	0.694	1.589
278.15	0.15	0.320	390.86	65.7	0.905	2.665	353.15	0.15	0.215	2559.40	82.6	0.682	1.551
278.15	0.20	0.391	416.58	66.5	0.901	2.572	353.15	0.20	0.275	2657.17	84.1	0.671	1.514
278.15	0.25	0.453	440.64	67.4	0.897	2.480	353.15	0.25	0.330	2750.80	85.7	0.659	1.477
278.15	0.30	0.506	463.19	68.3	0.893	2.391	353.15	0.30	0.382	2840.43	87.4	0.648	1.441
278.15	0.35	0.554	484.43	69.1	0.890	2.304	353.15	0.35	0.431	2926.20	89.1	0.637	1.406
278.15	0.40	0.597	504.42	69.9	0.887	2.218	353.15	0.40	0.478	3008.25	90.9	0.626	1.372
278.15	0.45	0.636	523.24	70.7	0.884	2.134	353.15	0.45	0.523	3086.85	92.8	0.615	1.339
278.15	0.50	0.672	541.10	71.5	0.881	2.052	353.15	0.50	0.567	3161.94	94.8	0.604	1.308
278.15	0.55	0.707	557.99	72.3	0.878	1.972	353.15	0.55	0.610	3233.78	96.8	0.594	1.277
278.15	0.60	0.740	573.99	73.1	0.876	1.893	353.15	0.60	0.652	3302.17	98.9	0.583	1.248
278.15	0.65	0.771	589.23	73.8	0.874	1.816	353.15	0.65	0.694	3367.33	101.0	0.573	1.221
278.15	0.70	0.803	603.77	74.5	0.872	1.741	353.15	0.70	0.736	3428.97	103.2	0.563	1.195
278.15	0.75	0.833	617.63	75.2	0.870	1.668	353.15	0.75	0.778	3486.95	105.3	0.554	1.170
278.15	0.80	0.865	630.80	75.8	0.868	1.596	353.15	0.80	0.821	3541.22	107.4	0.545	1.147
278.15	0.85	0.896	643.35	76.4	0.866	1.525	353.15	0.85	0.865	3591.27	109.4	0.536	1.126
278.15	0.90	0.929	655.21	77.0	0.865	1.456	353.15	0.90	0.909	3636.92	111.3	0.528	1.106
278.15	0.95	0.964	666.31	77.5	0.864	1.389	353.15	0.95	0.954	3677.73	113.1	0.521	1.087
278.15	1.00	1.000	676.65	78.0	0.863	1.323	353.15	1.00	1.000	3713.24	114.7	0.515	1.070
303.15	0.00	0.000	663.69	66.6	0.874	2.390							
303.15	0.05	0.109	715.95	67.5	0.867	2.319							
303.15	0.10	0.200	765.18	68.5	0.861	2.248							
303.15	0.15	0.278	811.44	69.4	0.855	2.179							
303.15	0.20	0.346	855.09	70.4	0.849	2.112							
303.15	0.25	0.405	896.25	71.4	0.844	2.046							
303.15	0.30	0.459	935.07	72.3	0.838	1.981							
303.15	0.35	0.508	971.75	73.3	0.833	1.917							
303.15	0.40	0.553	1006.50	74.3	0.828	1.855							
303.15	0.45	0.595	1039.38	75.3	0.823	1.795							
303.15	0.50	0.635	1070.62	76.2	0.819	1.736							
303.15	0.55	0.672	1100.27	77.2	0.814	1.679							
303.15	0.60	0.709	1128.53	78.1	0.810	1.623							
303.15	0.65	0.744	1155.35	79.1	0.806	1.568							
303.15	0.70	0.780	1180.93	80.0	0.803	1.515							
303.15	0.75	0.815	1205.13	80.8	0.799	1.464							
303.15	0.80	0.850	1228.16	81.7	0.796	1.413							
303.15	0.85	0.886	1249.81	82.5	0.793	1.365							
303.15	0.90	0.922	1270.08	83.2	0.790	1.317							
303.15	0.95	0.960	1288.84	83.9	0.788	1.271							
303.15	1.00	1.000	1305.94	84.6	0.786	1.226							

the fitting of the pure component parameters for propadiene was dependent on the mixture parameters for propadiene + propyne. This required an iteration between the fitting of the pure component parameters and the fitting of the mixture parameters until the changes in each parameter ceased to significantly affect the value of any of the other parameters.

Results

The "temperature-adjusted" results for mixtures of propyne with propane, propene, and propadiene are shown in Tables 2–4 along with the liquid phase compositions determined by the material balance. After parameters were fit to the model the same binary systems (without impurities) were predicted with bubble point calculations across the composition range. Tables 5–7 show the results from those calculations.

Figures 2–4 show the deviations from Raoult's law of both the results and fitted model. Figure 4 is not very useful for comparing the model's fit of the experimental data because the effects of the butane impurity in the propadiene are noticeable. This figure shows the differ-

Table 7. Calculated Liquid and Vapor Mole Fractions x_1 and y_1, Pressure, Liquid Molar Volume V^l, Vapor Compressibility Z, and Relative Volatility α for Propadiene (1) + Propyne (2)

T/K	x_1	y_1	P/kPa	V^l/(cm^3 mol^{-1})	Z	α	T/K	x_1	y_1	P/kPa	V^l/(cm^3 mol^{-1})	Z	α
253.15	0.00	0.000	115.56	59.9	0.950	1.855	328.15	0.00	0.000	1279.18	71.4	0.813	1.343
253.15	0.05	0.088	120.66	60.1	0.949	1.831	328.15	0.05	0.065	1306.76	71.6	0.810	1.329
253.15	0.10	0.167	125.55	60.2	0.949	1.806	328.15	0.10	0.128	1333.24	71.7	0.808	1.316
253.15	0.15	0.239	130.31	60.3	0.948	1.780	328.15	0.15	0.187	1358.61	71.9	0.806	1.303
253.15	0.20	0.305	134.86	60.4	0.948	1.754	328.15	0.20	0.244	1382.95	72.0	0.803	1.289
253.15	0.25	0.366	139.21	60.5	0.947	1.728	328.15	0.25	0.299	1406.32	72.2	0.801	1.277
253.15	0.30	0.422	143.41	60.6	0.947	1.701	328.15	0.30	0.351	1428.73	72.3	0.799	1.264
253.15	0.35	0.474	147.48	60.7	0.947	1.674	328.15	0.35	0.403	1450.24	72.4	0.797	1.251
253.15	0.40	0.523	151.34	60.8	0.946	1.647	328.15	0.40	0.452	1470.86	72.6	0.795	1.239
253.15	0.45	0.570	155.06	60.8	0.946	1.619	328.15	0.45	0.501	1490.65	72.7	0.793	1.227
253.15	0.50	0.614	158.65	60.9	0.946	1.591	328.15	0.50	0.549	1509.61	72.8	0.792	1.215
253.15	0.55	0.656	162.10	60.9	0.945	1.562	328.15	0.55	0.595	1527.74	72.8	0.790	1.204
253.15	0.60	0.697	165.41	60.9	0.945	1.534	328.15	0.60	0.641	1545.05	72.9	0.789	1.192
253.15	0.65	0.737	168.58	60.9	0.945	1.505	328.15	0.65	0.687	1561.66	73.0	0.787	1.181
253.15	0.70	0.775	171.61	60.9	0.945	1.475	328.15	0.70	0.732	1577.45	73.0	0.786	1.170
253.15	0.75	0.813	174.58	60.9	0.945	1.446	328.15	0.75	0.777	1592.48	73.1	0.785	1.159
253.15	0.80	0.850	177.33	60.9	0.945	1.416	328.15	0.80	0.821	1606.75	73.1	0.784	1.148
253.15	0.85	0.887	180.02	60.9	0.945	1.386	328.15	0.85	0.866	1620.34	73.1	0.783	1.137
253.15	0.90	0.924	182.64	60.8	0.945	1.356	328.15	0.90	0.910	1633.09	73.1	0.782	1.127
253.15	0.95	0.962	185.06	60.8	0.945	1.326	328.15	0.95	0.955	1645.09	73.1	0.781	1.117
253.15	1.00	1.000	187.40	60.8	0.945	1.296	328.15	1.00	1.000	1656.33	73.1	0.780	1.107
278.15	0.00	0.000	302.54	63.0	0.917	1.625	353.15	0.00	0.000	2239.69	78.5	0.717	1.247
278.15	0.05	0.078	312.75	63.1	0.916	1.605	353.15	0.05	0.061	2280.58	78.8	0.713	1.233
278.15	0.10	0.150	322.54	63.2	0.915	1.586	353.15	0.10	0.119	2319.33	79.0	0.710	1.220
278.15	0.15	0.217	331.98	63.3	0.914	1.566	353.15	0.15	0.176	2356.15	79.2	0.706	1.207
278.15	0.20	0.279	341.01	63.4	0.913	1.546	353.15	0.20	0.230	2391.10	79.4	0.703	1.196
278.15	0.25	0.337	349.77	63.5	0.912	1.525	353.15	0.25	0.283	2424.40	79.6	0.700	1.185
278.15	0.30	0.392	358.18	63.6	0.911	1.505	353.15	0.30	0.335	2456.12	79.8	0.697	1.174
278.15	0.35	0.444	366.18	63.6	0.910	1.484	353.15	0.35	0.385	2486.46	79.9	0.694	1.164
278.15	0.40	0.494	373.97	63.7	0.910	1.464	353.15	0.40	0.435	2515.41	80.0	0.691	1.155
278.15	0.45	0.541	381.35	63.7	0.909	1.443	353.15	0.45	0.484	2543.20	80.1	0.689	1.147
278.15	0.50	0.587	388.52	63.8	0.908	1.422	353.15	0.50	0.532	2569.81	80.2	0.686	1.139
278.15	0.55	0.631	395.35	63.8	0.908	1.401	353.15	0.55	0.580	2595.32	80.3	0.684	1.131
278.15	0.60	0.674	401.90	63.8	0.907	1.380	353.15	0.60	0.628	2619.87	80.3	0.682	1.124
278.15	0.65	0.716	408.17	63.8	0.907	1.358	353.15	0.65	0.675	2643.45	80.4	0.680	1.118
278.15	0.70	0.757	414.17	63.8	0.906	1.337	353.15	0.70	0.722	2666.13	80.4	0.678	1.112
278.15	0.75	0.798	419.96	63.8	0.906	1.315	353.15	0.75	0.769	2688.06	80.5	0.676	1.106
278.15	0.80	0.838	425.41	63.8	0.906	1.293	353.15	0.80	0.815	2709.23	80.5	0.674	1.101
278.15	0.85	0.878	430.58	63.8	0.905	1.271	353.15	0.85	0.861	2729.63	80.5	0.672	1.097
278.15	0.90	0.918	435.54	63.7	0.905	1.248	353.15	0.90	0.908	2749.49	80.5	0.670	1.092
278.15	0.95	0.959	440.16	63.7	0.905	1.226	353.15	0.95	0.954	2768.73	80.5	0.669	1.088
278.15	1.00	1.000	444.50	63.6	0.905	1.203	353.15	1.00	1.000	2787.41	80.6	0.667	1.085
303.15	0.00	0.000	663.69	66.6	0.874	1.460							
303.15	0.05	0.071	681.20	66.7	0.872	1.445							
303.15	0.10	0.137	698.09	66.8	0.871	1.430							
303.15	0.15	0.200	714.37	67.0	0.869	1.415							
303.15	0.20	0.259	730.02	67.1	0.868	1.400							
303.15	0.25	0.316	745.12	67.2	0.866	1.384							
303.15	0.30	0.370	759.60	67.3	0.865	1.369							
303.15	0.35	0.422	773.52	67.4	0.863	1.353							
303.15	0.40	0.471	786.97	67.4	0.862	1.338							
303.15	0.45	0.520	799.79	67.5	0.861	1.322							
303.15	0.50	0.566	812.13	67.6	0.860	1.306							
303.15	0.55	0.612	823.99	67.6	0.859	1.290							
303.15	0.60	0.657	835.30	67.7	0.858	1.274							
303.15	0.65	0.700	846.06	67.7	0.857	1.258							
303.15	0.70	0.744	856.33	67.7	0.856	1.242							
303.15	0.75	0.786	866.12	67.8	0.856	1.226							
303.15	0.80	0.829	875.43	67.8	0.855	1.209							
303.15	0.85	0.871	884.18	67.7	0.855	1.193							
303.15	0.90	0.914	892.39	67.7	0.854	1.176							
303.15	0.95	0.957	900.11	67.7	0.854	1.159							
303.15	1.00	1.000	907.21	67.7	0.854	1.142							

ences in the deviations from Raoult's law of the fitted model for the binary propadiene + propyne system with those of the experimental ternary propadiene + propyne + butane system. The butane + propadiene and butane + propyne interactions were estimated to be equal to the propane + propadiene interactions as measured by Burcham (1981, 1986) assuming a similar alkane + diolefin interaction. These interactions caused an additional 0.5% maximum deviation in the experimental propadiene + propyne results. Since these interactions were estimated, the results for the propadiene + propyne binary system have additional uncertainty.

Although the identity of the propadiene impurities was determined to be different from that reported by Burcham (1986), which changed the values for the pure component vapor pressures, it was not observed to have a large effect in either the binary interactions or the relative volatilities.

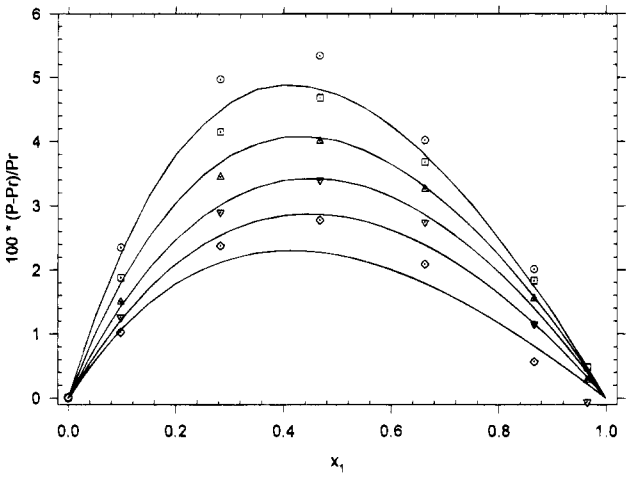

Figure 4. Comparison of the Raoult's law pressure deviations for experimental data and the model for propadiene (1) + propyne (2): dotted circle, 253.15 K; dotted square, 278.15 K; dotted triangle, 303.15 K; dotted inverted triangle, 328.15 K; dotted tilted square, 353.15 K. The fit appears poor because the prediction is for pure binary mixtures but experimental results have an influence of 3.8 mol % butane from pure propadiene.

Conclusions

An accurate T, P, x_i data set has been reported for the propane + propyne, propene + propyne, and propadiene + propyne systems for the temperature range of 253.15–353.15 K. An equation of state model was used to obtain the liquid and vapor phase compositions. These results should be useful in evaluating the alkyne interactions with alkanes, alkenes, and diolefins of light hydrocarbons.

Literature Cited

Ambrose, D. The Correlation and Estimation of Vapour Pressures IV. Observations on Wagner's Method of Fitting Equations to Vapour Pressures. *J. Chem. Thermodyn.* **1986**, *18*, 45–51.

Barclay, D. A. Relative Volatility of the Ethane-Ethylene System. Ph.D. Dissertation, University of Missouri—Rolla, Rolla, MO, 1980.

Bondar, A. M.; Mushii, R. Ya.; Kostyuk, V. N.; Moshkovich, F. B. The Conditions for the Explosive Decomposition of Allene. *Khim. Promst. (Moscow)* **1965**, *41*, 923–924 (in Russian).

Burcham, A. F. Vapor Pressures for the Propane-Propadiene System. M.S. Thesis, University of Missouri—Rolla, Rolla, MO, 1981.

Burcham, A. F.; Trampe, M. D.; Poling, B. E.; Manley, D. B. In *Phase Equilibria for the Propane-Propadiene System from Total Pressure Measurements, Equations of State / Theories and Applications*; Chao, K. C., Robinson, R. L., Jr., Eds. *ACS Symp. Ser.* **1986**, *300*, 86–107.

Flebbe, J. L. Vapor Pressures of Some C-4 Hydrocarbons and Their Mixtures. Ph.D. Dissertation, University of Missouri—Rolla, Rolla, MO, 1980.

Huston, R. F.; Barrios, C. A.; Holleman, R. A. Weathering and Stability of Methylacetylene-Propadiene-Hydrocarbon Mixtures. *J. Chem. Eng. Data* **1970**, *15*, 168–173.

Kuchta, J. M.; Spolan, I.; Zabetakis, M. G. Flammability Characteristics of Methylacetylene, Propadiene (Allene), and Propylene Mixtures. *J. Chem. Eng. Data* **1964**, *9*, 467–472.

Kyser, E. A., III. Experimental Vapor-Liquid Equilibria of Propyne with Propane, Propene and Propadiene. Ph.D. Dissertation, University of Missouri—Rolla, Rolla, MO, 1987.

Panagiotopoulos, A. Z.; Reid, R. C. Multiphase High Pressure Equilibria in Ternary Aqueous Systems. *Fluid Phase Equilib.* **1986**, *29*, 525–534.

Peneloux, A.; Rauzy, E.; Freze, R. A Consistent Correction for Relich-Kwong-Soave Volumes. *Fluid Phase Equilib.* **1982**, *8*, 7–23.

Rutledge, T. F. *Acetylenic Compounds*; Reinhold Book Corp.: New York, 1968.

Van Hook, W. A. Vapor Pressures of the Methylacetylenes, H3CCCH, H3CCCD, D3CCH, and D3CCCD. *J. Chem. Phys.* **1967**, *46*, 1907–1918.

Vidaurri, F. C. Vinyl Acetylene Binary Activity Coefficients with C4-unsaturates. *J. Chem. Eng. Data* **1975**, *20*, 328–333.

Yoshimine, M.; Kern, W. G.; Belfit, R. W., Jr. Stabilization of Methylacetylene and Propadiene Mixtures. *J. Chem. Eng. Data* **1967**, *12*, 399–405.

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