

Vinyl Acetylene Binary Activity Coefficients with C₄-Unsaturates

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Binary vapor-liquid equilibrium data were obtained for dilute mixtures (<18 mol %) of vinyl acetylene in *cis*-butene-2, in *trans*-butene-2, and in 1,3-butadiene. Studies were made in the dilute region to permit accurate estimations of infinite dilution activity coefficients and because of the hazardous nature of mixtures containing high concentrations of vinyl acetylene. High-precision data were obtained and successfully regressed to Wilson-type activity coefficient equations. The regressed equations and required auxiliary equations accurately predicted vapor compositions, matching the experimental compositions to an average of about 1% deviation. Infinite dilution activity coefficients calculated from the Wilson equations coincided with those calculated from regular solution theory for the vinyl acetylene-1,3-butadiene binary but were about 20% higher than regular solution predictions for the other two binaries. At 110.5°F the systems of equations predicted low-boiling binary azeotropes for the systems vinyl acetylene-*trans*-butene-2 and vinyl acetylene-*cis*-butene-2.

Chemical equilibrium quantities of vinyl acetylene are generated in the commercial production of 1,3-butadiene. The vinyl acetylene is an undesirable contaminant, and its concentration in the butadiene must be lowered to an industrially acceptable level. A knowledge of the physical equilibrium relationships between vinyl acetylene and other C₄-unsaturates will permit design options to be studied that will result in increased efficiency in the butadiene purification process. The C₄-unsaturates considered in this study were *cis*- and *trans*-butene-2 and 1,3-butadiene.

Studies were made in the region of dilute concentrations of vinyl acetylene to permit accurate estimation of infinite dilution activity coefficients and because of the hazardous nature of mixtures containing high concentrations of vinyl acetylene. Special precautions were taken in selecting the experimental region to be studied, in the materials used in the experimental apparatus, in the quantities of hydrocarbons that were used, and in the storage, handling, transfer, and disposal of samples.

Experimental

Materials. Phillips Petroleum Co. research grade (99.7 minimum mol %) *cis*- and *trans*-butene-2 and special purity (99.5 minimum mol %) 1,3-butadiene were used in this study. The monovinyl acetylene (1-buten-3-yne) was obtained from the Chemical Samples Co. The vinyl acetylene was received as a 50% solution by weight in xylene, containing 0.05% by weight *p*-tertiary-butyl catechol. The vinyl acetylene contained up to 2% impurities prior to storage in the xylene.

Apparatus and procedure. The experimental apparatus consisted of a Jurgeson gauge used as an equilibrium cell in a thermostated water bath, a vapor recirculating pump, and an accurate Heise gauge maintained and calibrated at 120°F. Provisions were made for taking direct vapor samples (six or seven) to a sample valve feeding a Carle Model 8000 gas chromatograph having thermistor detectors. The chromatograph was equipped with a 1/8-in. × 10-ft stainless-steel column packed with 9.1 wt % bis-(2-methyl ethyl) adipate on

acid washed DMCS treated 80/100 mesh Chromasorb P. The column was maintained at 100°C and had a helium flow rate of 30 cc/min. Peak area integration was performed by a centrally located IBM 1800 computer. Response factors were determined by gas standards made up by pressure addition and checked by weight gained by the sample cylinders.

Two liquid samples from the equilibrium cell were taken in a previously flushed and evacuated 0.2-cc sample loop and then transferred to 300-cc sample cylinders by immersing the cylinders in liquid nitrogen. The ratio of the sample cylinder volume to the sample loop volume insured that the liquid sample would be totally vaporized when reheated back up to room temperature. Pressures in the sample cylinders were monitored to ascertain that the total pressure was always below the vapor pressure of the pure heavy component (vinyl acetylene). The sample cylinders were provided with glass beads to mix the sample vapors as the cylinders were mechanically rotated and warmed back up by controlled use of a heat lamp. Five or six chromatographic determinations were made on each liquid sample.

Safety. Monovinyl acetylene is a very dangerous material to handle. Seven areas of safety were considered and are discussed below.

Under certain conditions it will form extremely explosive acetylides in the presence of copper or copper-bearing alloys, silver, mercury, or the salts of these metals. No brass pressure gauges were used (even on the pressure gauge on the sample loop for the chromatograph). No mercury manometers were used to interface the equilibrium cell to the Heise pressure gauge.

Vinyl acetylene forms explosive mixtures with air over a wide range of concentrations. The equilibrium cell system was evacuated and repressured with oxygen free nitrogen three times before the vinyl acetylene was charged. The cell was chilled to ice temperature at the last evacuation. The required vinyl acetylene was charged at this time (by weight loss, sampled from the vapor phase of the vinyl acetylene-xylene container), followed by the addition of the other unsaturated C₄ hydrocarbon under study. The bath was then brought up to the desired temperature and equilibrated for at least 1 hr prior to sampling.

Vinyl acetylene becomes extremely unstable at temperatures above 212°F. Maximum temperature in this study was 110.5°F. All samples containing vinyl acetylene were stored at 32°F.

Vinyl acetylene can be exploded in absence of air if strongly enough incited (i.e., electrical spark), especially under pressure. The safety region (Figure 1) as determined by Ritzert and Berthold (13) was used in selecting conservatively safe combinations of vinyl acetylene concentration, temperature, and pressure to investigate.

Vinyl acetylene forms peroxides in the presence of air, and they are violently explosive. An iodide test on the as received vinyl acetylene indicated the presence of a low concentration of peroxides. Additional *p*-tertiary-butyl catechol was added to the xylene mixture to suppress further peroxide formation. A judgment was made that to remove the peroxides might be more dangerous than to work carefully knowing that they were present. A peroxide removal step yields concentrated vinyl acetylene that is more unstable and readily forms more

peroxides, and a concentrated quantity of peroxides to be disposed of properly. The hydrocarbon mixtures in the equilibrium cell were never evaporated to dryness. The mixtures in the cell were diluted with xylene before being drained to a liquid nitrogen-chilled container holding additional xylene. Additional xylene flushes of the cell were similarly added to the disposal container. The containers were tagged for disposal by burning, handled by the Phillips Safety Department. The cell was then rinsed several times with acetone and evacuated to dryness in preparation for the next run.

Vinyl acetylene gradually polymerizes during storage. The polymers can also be peroxidized. All vinyl acetylene transfers were made from the vapor phase, leaving the possible higher molecular-weight material behind. Similar polymerizations can occur with 1,3-butadiene, and it was similarly transferred from the vapor phase after analyzing and properly degassing light contaminants from the vapor phase. All vinyl acetylene samples were dated when received and when used. Only small quantities (two 25-gram samples of vinyl acetylene) were kept on hand. A maximum of one-half of the vinyl acetylene was used from each xylene mixture, the rest being discarded through the Safety Department. It is estimated that the vapor-phase transfer of vinyl acetylene resulted in a transfer of 0.2 mol % xylene in the vinyl acetylene with a new xylene mixture and about 0.6 mol % xylene at the time the mixture was discarded.

Quantities of vinyl acetylene charged to the equilibrium cell were very small. A maximum of 8 grams of vinyl acetylene was used at the higher concentrations. The equilibrium cell had a pressure rating of 2380 psig, but the pressure-limiting parts of the apparatus were the 100 and 300 psia Heise gauges that were used. The experimental apparatus was assembled in a safety hood. The equilibrium cell was shielded by the open top metal wall water bath and a portable Plexiglas shield. The pressure gauges were mounted above the level that the hood safety glass would be opened during sampling. The Carle chromatograph was also located in the safety hood to minimize the lengths of connecting tubing.

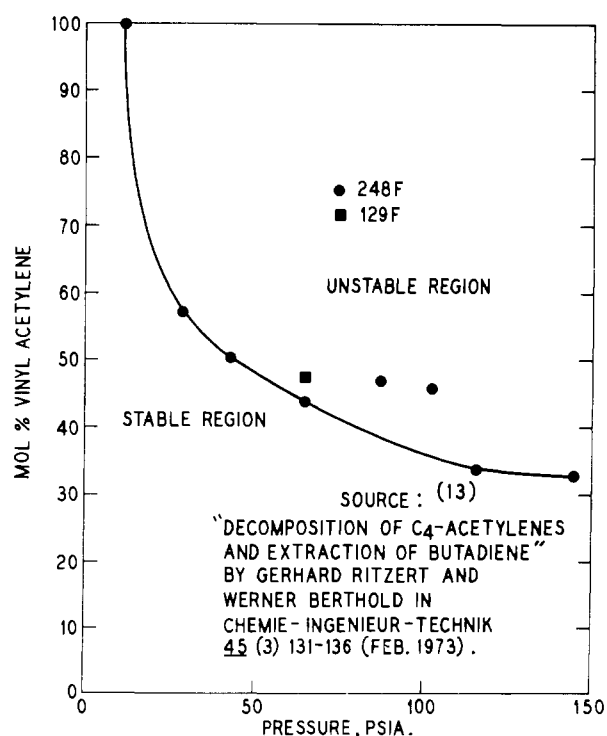


Figure 1. Stability of vinyl acetylene vapors with ignition source

Experimental Data

Binary vapor-liquid equilibrium measurements were made on vinyl acetylene with *cis*-butene-2, with *trans*-butene-2, and with 1,3-butadiene. Dilute mixtures of vinyl acetylene were used to allow accurate determination of infinite dilution activity coefficients or model parameters from which infinite dilution activity coefficients could be determined. Infinite dilution activity coefficients (or their equivalent) can be successfully used to predict solution deviation from ideality over the entire composition range.

The variables that were measured were temperature and liquid composition. The measured responses were pressure and vapor composition. The experimental measurements are presented in Tables I-III. Since replicate samples were taken of each phase at equilibrium, estimates of the precision of the composition measurements are available. The precision is reported as percent relative error. The calculated point values of the activity coefficients are also presented in these tables. In some instances, activity coefficients as low as 0.995 are calculated for the major component. These are a result of an experimental pressure that is slightly too low or a pure component vapor pressure that is slightly too high as predicted by the vapor-pressure equation.

Data Reduction and Regression

Using the experimental P , T , x , and y data, liquid-phase activity coefficients, γ_i , were calculated from

$$\gamma_i = \frac{y_i P \phi_i}{x_i \bar{f}_i} \quad (1)$$

Vapor-phase fugacity coefficients, ϕ_i , were determined using the Redlich-Kwong equation of state (12). The standard state liquid fugacities, \bar{f}_i , were obtained from

$$\bar{f}_i = P_i^s \phi_i^s \quad (2)$$

where the vapor fugacity coefficients for the pure components, ϕ_i^s , were obtained from the Redlich-Kwong equation evaluated at the system temperature and the pure component saturation pressure, P_i^s .

The saturation pressures were obtained from equations having the form

$$\ln P_i^s = C_1 + \frac{C_2}{T} + C_3 T + C_4 \ln T \quad (3)$$

Constants for these equations are listed in Table IV. These constants were obtained by regression analysis from data obtained from the sources indicated.

Pure component liquid volumes are required for activity coefficient models. The effect of temperature on pure component liquid molar volume, v_i^L , was determined from equations of the form

$$v_i^L = a + bT + cT^2 \quad (4)$$

Constants for these equations are given in Table V. The constants were determined from correlations using data from the indicated sources.

The Wilson equation (15) was chosen to correlate the reduced experimental data. It is superior to older equations (7) in modeling vapor-liquid equilibrium data where only one liquid phase is present. It has the added advantage that only binary parameters are required for the prediction of activity coefficients in multicomponent systems.

In the binary form of the equation, the activity coefficients are calculated from

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (5)$$

and

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (6)$$

The two constants (Λ_{12} and Λ_{21}) for each binary pair are determined from the equations

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp \left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \quad (7)$$

A regressed parameter is associated with each of the Λ constants, viz., $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$. Values of these (Wilson) parameters are those which minimize the objective function, β .

$$\beta = \sum_{i=1}^n [(\gamma_{1,i}^{(\text{obsd})} - \gamma_{1,i}^{(\text{calcd})})^2 + (\gamma_{2,i}^{(\text{obsd})} - \gamma_{2,i}^{(\text{calcd})})^2] \quad (8)$$

After the Wilson parameters were established, infinite dilution activity coefficients were calculated from

$$\ln \gamma_1^\infty = 1 - \ln \Lambda_{12} - \Lambda_{21} \quad (5a)$$

and

$$\ln \gamma_2^\infty = 1 - \ln \Lambda_{21} - \Lambda_{12} \quad (6a)$$

Results

Simultaneous regression of multitemperature isothermal data. Vapor-liquid equilibrium measurements were taken at three temperature levels for the binaries vinyl acetylene-*cis*-butene-2 and vinyl acetylene-*trans*-butene-2. Measurements were taken at two temperature levels for the vinyl acetylene-1,3-butadiene system. All of the data for a given binary were regressed simultaneously in an attempt to obtain values of the regressed parameters which reflected the correct temperature dependence. Individual data points were not weighed

Table I. Phase Equilibria for Vinyl Acetylene-*cis*-Butene-2

Temp, °F	Press, psia	Liquid		Vapor		% Dev ^c of calcd VA vapor compn	Activity coefficients	
		Compn mol % vinyl acetylene	Exptl ^{a,b} % rel error	Compn mol % vinyl acetylene	Exptl ^{a,b} % rel error		Vinyl acetylene	<i>cis</i> -Butene-2
40.7	15.7	10.01	1.10	12.17	2.32	0.70	1.313	0.995
40.7	15.8	12.19	3.24	14.60	1.50	0.69	1.302	0.997
40.7	15.8	14.77	0.60	17.57	1.29	1.73	1.293	0.992
90.5	39.2	1.96	0.59	2.52	1.20	0.73	1.334	0.989
90.5	39.7	5.43	0.75	6.88	0.37	1.71	1.329	0.992
90.5	40.0	9.41	0.51	11.49	0.39	0.86	1.290	0.991
90.5	40.4	12.71	0.39	15.02	0.32	-0.12	1.262	0.996
110.5	54.7	2.00	1.45	2.49	1.30	-1.00	1.307	0.997
110.5	55.0	5.47	1.22	6.77	0.51	0.74	1.304	0.993
110.5	55.5	9.41	0.61	11.44	0.74	1.55	1.291	0.992
110.5	56.0	12.73	0.39	14.97	0.23	0.33	1.259	0.997
			Av = 0.99		Av = 0.92	Av = 0.92		

^a % Relative error = $\left(\frac{\sigma_x}{\bar{x}} \text{ or } \frac{\sigma_y}{\bar{y}} \right) (100)$. ^b % Relative error for component 2 = (% relative error for component 1) $\left(\frac{\bar{x}_1}{\bar{x}_2} \text{ or } \frac{\bar{y}_1}{\bar{y}_2} \right)$. ^c % Deviation = $\frac{(y_{\text{measd}} - y_{\text{calcd}})}{y_{\text{measd}}} (100)$.

Table II. Phase Equilibria for Vinyl Acetylene-*trans*-Butene-2

Temp, °F	Press, psia	Liquid		Vapor		% Dev ^c of calcd VA vapor compn	Activity coefficients	
		Compn mol % vinyl acetylene	Exptl ^{a,b} % rel error	Compn mol % vinyl acetylene	Exptl ^{a,b} % rel error		Vinyl acetylene	<i>trans</i> -Butene-2
37.2	15.7	4.84	1.40	5.87	1.10	-2.83	1.412	1.001
37.2	15.8	6.13	0.97	7.56	0.77	0.34	1.443	1.003
37.2	16.0	7.95	0.73	9.61	1.31	0.60	1.434	1.012
90.5	42.9	1.56	1.77	2.01	1.42	-1.53	1.449	1.018
90.5	42.9	3.83	0.81	4.77	0.23	-1.99	1.406	1.015
90.5	42.7	7.24	0.56	8.82	0.33	-0.35	1.369	1.002
90.5	43.6	14.40	0.24	16.42	0.40	-0.01	1.305	1.013
110.5	58.9	1.48	3.05	1.90	1.84	-0.70	1.438	1.014
110.5	59.2	3.87	1.58	4.81	0.23	-1.20	1.399	1.013
110.5	59.2	7.22	0.40	8.68	0.63	-0.98	1.353	1.007
110.5	59.7	14.14	0.42	16.02	0.59	-0.41	1.286	1.009
			Av = 1.08		Av = 0.80	Av = 0.99		

^a % Relative error = $\left(\frac{\sigma_x}{\bar{x}} \text{ or } \frac{\sigma_y}{\bar{y}} \right) (100)$. ^b % Relative error for component 2 = (% relative error for component 1) $\left(\frac{\bar{x}_1}{\bar{x}_2} \text{ or } \frac{\bar{y}_1}{\bar{y}_2} \right)$. ^c % Deviation = $\frac{(y_{\text{measd}} - y_{\text{calcd}})}{y_{\text{measd}}} (100)$.

in proportion to precision of the measurement. The regression technique operated on the activity coefficients. This prevented all of the experimental errors from being lumped into the vapor-phase composition.

Regressed parameter values for each binary pair that was studied are listed in Table VI. These parameters were used to predict activity coefficients for the binaries. Predicted values for vinyl acetylene activity coefficients at 110.5°F are plotted on an expanded scale in Figure 2. Also plotted are the activity coefficients calculated from the experimental data. Vapor compositions were predicted for the experimental liquid compositions. Comparisons of the experimental and calculated vapor compositions are presented in Tables I-III with the experimental data.

Estimation of goodness of fit. Statistical tests which are

applicable to linear models are not appropriate with nonlinear models (2). Practically, however, an approximate idea of the lack of fit of the model can be obtained by comparing the lack of fit mean square against the pure error estimate of the standard deviation. In terms of the tabulated data, the lack of fit mean square is obtained from

$$MS_{LF} = \frac{S(\lambda_{12}, \lambda_{21})}{k-2} = \frac{\sum_{i=1}^k \left[\left(\frac{\% \text{ Deviation}}{100} \right)_i \bar{y}_i \right]^2}{k-2} \quad (9)$$

where k is the number of experimental points. The lack of fit mean square is obtained directly since the replicate data were averaged prior to regression. $k-2$ degrees of freedom are associated with this mean square since two degrees were utilized in the estimation of the two Wilson parameters.

Table III. Phase Equilibria for Vinyl Acetylene-1,3-Butadiene

Temp, °F	Press, psia	Liquid		Vapor		% Dev ^c of calcd VA vapor compn	Activity coefficients	
		Compn mol % vinyl acetylene	Exptl ^{a,b} % rel error	Compn mol % vinyl acetylene	Exptl ^{a,b} % rel error		Vinyl acetylene	1,3-Butadiene
90.5	50.9	1.88	2.10	1.75	2.62	-1.01	1.227	1.001
90.5	50.3	3.36	1.36	3.09	1.30	-1.83	1.199	0.992
90.5	50.2	7.54	1.29	7.13	0.61	2.34	1.233	0.992
90.5	49.7	9.13	0.84	8.52	0.60	1.53	1.206	0.985
110.5	68.9	1.28	1.65	1.23	2.57	1.35	1.241	0.993
110.5	68.8	3.34	0.96	3.12	0.66	-0.80	1.205	0.994
110.5	68.5	7.49	0.73	7.07	0.31	1.31	1.212	0.992
110.5	68.1	9.09	0.71	8.54	0.48	1.26	1.199	0.989
			Av = 1.21		Av = 1.14	Av = 1.43		

^a % Relative error = $\left(\frac{\sigma_x}{\bar{x}} \text{ or } \frac{\sigma_y}{\bar{y}} \right) (100)$. ^b % Relative error for component 2 = (% relative error for component 1) $\left(\frac{\bar{x}_1}{\bar{x}_2} \text{ or } \frac{\bar{y}_1}{\bar{y}_2} \right)$. ^c % Deviation = $\frac{(y_{\text{measd}} - y_{\text{calcd}})}{y_{\text{measd}}} (100)$.

Table IV. Constants of Vapor-Pressure Equation^a

	C ₁	C ₂	C ₃	C ₄	Ref
Vinyl acetylene	218.51	-9171.7	0.047713	-35.325	5, 9, 10
cis-Butene-2	86.814	-5167.1	0.017706	-12.990	1, 14
trans-Butene-2	67.6874	-4467.25	0.0145179	-9.8670	5, 8
1,3-Butadiene	99.1612	-5291.80	0.022403	-15.2825	4, 10

^a P^s in atm, T in K.

Table V. Constants of Volume Equation^a

	a	b	c	Ref
Vinyl acetylene	83.633	-0.20462	0.00058962	9
cis-Butene-2	281.05	-1.4242	0.0026128	3
trans-Butene-2	304.194	-1.53086	0.0027581	3
1,3-Butadiene	254.265	-1.26099	0.0023326	4

^a v in cc/g-mol, T in K.

Table VI. Wilson Parameters

Binary mixtures with vinyl acetylene component 1

	$\lambda_{12} - \lambda_{11}$	$\lambda_{21} - \lambda_{22}$
cis-Butene-2	-68.1358	-164.872
trans-Butene-2	-373.090	140.189
1,3-Butadiene	-58.3578	-99.7270

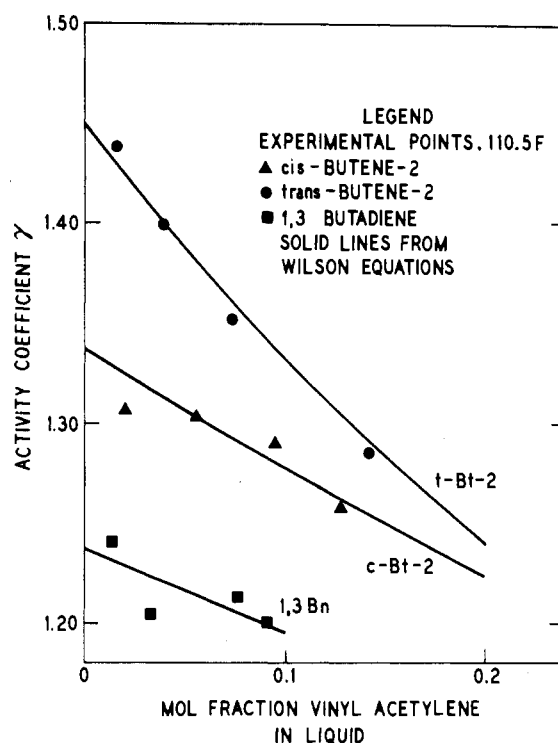


Figure 2. Activity coefficient of vinyl acetylene with C₄-unsaturates

The pure error mean square is calculated from

$$S_e = \frac{\sum_{i=1}^k \left[\left(\frac{\% \text{ relative error in } \bar{y}_i}{100} \right) \bar{y}_i \right]^2}{k} \quad (10)$$

There are 5 k degrees of freedom associated with the pure error mean square since at least six vapor samples were taken at each experimental condition. A ratio of the lack of fit mean square to the pure error mean square yields

$$\frac{MS_{LF}}{S_e} = \frac{\sum_{i=1}^k [(\% \text{ Deviation})_i \bar{y}_i]^2 (k)}{\sum_{i=1}^k [(\% \text{ relative error in } \bar{y}_i) \bar{y}_i]^2 (k - 2)} \quad (11)$$

with $k-2$ degrees of freedom for the numerator and 5 k for the denominator.

These calculations were carried out for vapor-phase compositions of vinyl acetylene, since the bulk of derived activity coefficient information (the quantities that were regressed) was for this component. Activity coefficients for the second (major) components remained close to one (as expected) over the experimental range. Values of the calculated ratios are presented in Table VII and are compared to the corresponding F ratio for a rough comparison. The Wilson models appear to predict vinyl acetylene vapor-phase concentration within the accuracy of the experimental data for the vinyl acetylene-*cis*-butene-2 and the vinyl acetylene-*trans*-butene-2 binaries. The binary with 1,3-butadiene is apparently not fit within the experimental error associated with the vapor phase, although the fit is good (average relative error 1.4%, maximum relative error 2.3%).

Comparison to regular solution theory. Since all of the experimental data were obtained in the dilute vinyl acetylene region, several checks were made on the regressed values for the Wilson parameters. Infinite dilution activity coefficients were calculated for vinyl acetylene and the C_4 -unsaturates from Equations 5a and 6a. These values are listed in Table

Table VII. Correlation Error
Binary with vinyl acetylene as component 1

	Range of exptl y_1 mol %	Av % error ^a in calcd y_1	Error sum ^b of squares	MS_{LF} ^c S_e	F
<i>cis</i> -Butene-2	2.5-17.6	0.92	0.00293	1.069	2.06 ^d
<i>trans</i> -Butene-2	1.9-16.4	0.99	0.00491	1.644	2.06 ^d
1,3-Butadiene	1.2-8.5	1.43	0.00423	7.84	2.34 ^e

^a % Error = $\left[\frac{y_{\text{exptl}} - y_{\text{calcd}}}{y_{\text{exptl}}} \right] (100)$. ^b Minimum value of Equation 8. ^c From Equation 11. ^d $F(9, 55, 0.05)$. ^e $F(6, 40, 0.05)$.

Table VIII. Infinite Dilution Activity Coefficients^a

	Soly parameter, (cal/cc) ^{1/2}	Molar vol, cc/g-mol @ 25°C	Vinyl acetylene inf diln activity coeff in C_4 -unsat		C_4 -unsat inf diln activity coeff in vinyl acetylene	
			Wilson equation	Reg soln	Wilson equation	Reg soln
Vinyl acetylene	8.25	75.1				
<i>cis</i> -Butene-2	7.25	91.2	1.337	1.127	1.446	1.156
<i>trans</i> -Butene-2	7.03	93.8	1.448	1.194	1.356	1.248
1,3-Butadiene	6.94	88.0	1.238	1.227	1.285	1.271

^a At 110.5°F.

VIII. From regular solution theory (δ), the infinite dilution activity coefficients of a binary can be calculated from

$$RT \ln \gamma_A^\infty = v_A [\delta_A - \delta_B]^2 \quad (12)$$

where v_A is the pure component molar volume, and δ_A and δ_B are solubility parameters. Regular solution infinite dilution coefficients were calculated and are also reported in Table VIII. Experimental infinite dilution activity coefficients as determined from the Wilson parameters coincided with those calculated from regular solution theory for the vinyl acetylene-1,3-butadiene system. At 110.5°F, the experimental infinite dilution coefficient for vinyl acetylene was 19% higher than regular solution theory prediction for the vinyl acetylene-*cis*-butene-2 system and 21% higher for the vinyl acetylene-*trans*-butene-2 binary. Prausnitz (17) has stated that "solubility-parameter theory is not quantitatively reliable for components whose solubility parameters are very nearly the same." For these systems, it cannot be established a priori how good the regular solution predictions will be.

Qualitatively, regular solution theory predicts that infinite dilution activity coefficients of a binary are related by

$$\gamma_B^\infty = \gamma_A^\infty \left(\frac{v_B}{v_A} \right) \quad (13)$$

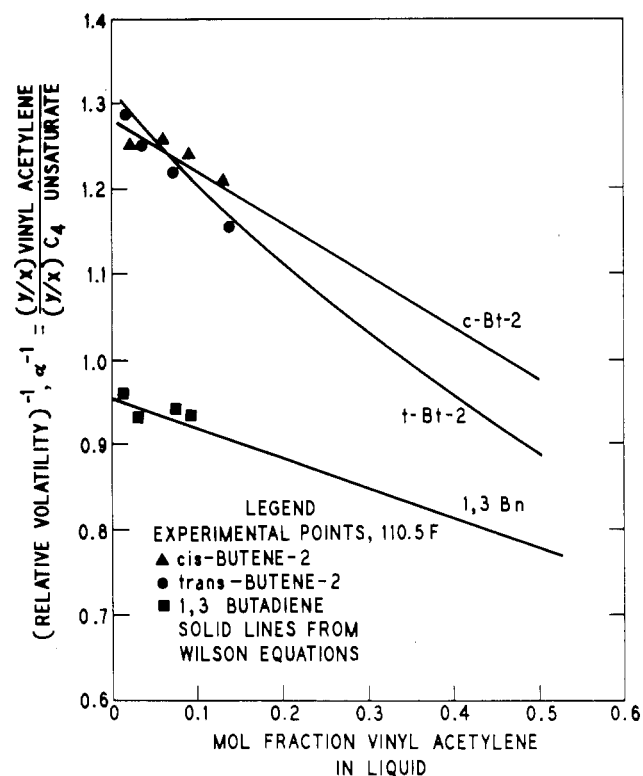


Figure 3. Relative volatility of vinyl acetylene with C_4 -unsaturates

establishing which of the infinite dilution coefficients should be the largest. An exact matching of this relationship was not expected since no data were obtained in the dilute C₄-unsaturated region. The vinyl acetylene-*cis*-butene-2 and vinyl acetylene-1,3-butadiene binaries adhered to the above relationship, whereas the vinyl acetylene-*trans*-butene-2 did not. Attempts to incorporate Equation 13 as a constraint in the *trans*-butene-2 system proved unsuccessful, the resulting *F* ratio being 15 times larger than with the original Wilson parameters (although the average % relative error in calculating the vapor composition only increased from 1 to 2.6 %).

Regular solution theory predicts that the temperature variation of infinite dilution activity coefficients can be obtained from

$$\gamma_1^\infty = \gamma_2^\infty \left(\frac{v_1 T_2}{v_2 T_1} \right) \quad (14)$$

For all three binaries, the Wilson equations were in agreement with regular solution theory in predicting the temperature dependence of the infinite dilution activity coefficients.

Prediction of binary azeotropes. The Wilson equations were used to generate relative volatilities for each binary. These are presented in Figure 3 for a temperature of 110.5°F. This plot shows that at 34 mol %, vinyl acetylene forms a low-boiling azeotrope with *trans*-butene-2. Similarly at 46 mol %, vinyl acetylene forms a low-boiling azeotrope with *cis*-butene-2. Note that these predicted azeotropes are outside the range of the experimental data. A degree of uncertainty exists as to the actual composition of the azeo-

tropes, since, experimentally, little information was generated for the activity coefficients of the C₄-unsaturates in vinyl acetylene.

Acknowledgment

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Vapor-Liquid Equilibrium Relationships of Binary Systems *n*-Butane-*n*-Pentane and *n*-Butane-*n*-Hexane

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The *P*-*ρ*-*T*-*x* relationships of the *n*-butane-*n*-pentane and *n*-butane-*n*-hexane systems are determined. The experimental results cover a range from about 100 lb/in.² abs and room temperature to the highest pressure and temperature at which liquid and vapor can coexist. The data are presented in tabular form. *P*-*T*-*x*, *ρ*-*T*-*x*, and isobaric *T*-*x* diagrams are given.

This experimental study reports the *P*-*ρ*-*T*-*x* relationships along the liquid-vapor phase boundaries of the binary systems of *n*-pentane and *n*-hexane with *n*-butane as the common component. It is the fourth of a series of studies (4-6) whose primary object has been to explore the effect of the relative size of the components of a binary system on its phase diagram in the liquid-vapor region.

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Experimental

The *P*-*ρ*-*T*-*x* relationships of the two *n*-butane-*n*-alkane systems were obtained by the determination of the *P*-*T* and *V*-*T* border curves of a series of mixtures of known composition. The relationships between any set of the variables were then obtained by appropriate cross plots of these curves.

The apparatus and experimental procedures employed were the same as those employed in the studies previously reported (4-6). Very briefly, the operation consisted in confining a measured amount of an air-free sample over mercury in a glass capillary tube, hereafter referred to as the experimental tube, which was fastened in one leg of a mercury-in-steel, U-tube. The other leg was connected through a manifold to a compressed gas cylinder which served as a source of pressure and to a sensitive spring gauge for the measurement of the applied pressure. The tube was surrounded by a constant-temperature jacket whose temperature was measured by means of a copper-constantan thermocouple in conjunction with a potentiometer. By a precalibration of the experi-