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A Nonlinear Correlation of High-Pressure Vapor–Liquid Equilibrium Data for Ethylene + *n*-Butane Showing Inconsistencies in Experimental Compositions[1]

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The modified Leung–Griffiths model is applied to the previously unpublished data, tabulated here, of Williams for high-pressure vapor–liquid equilibria of ethylene + *n*-butane. It is not possible to obtain a highly accurate correlation with the experimentally stated compositions, but evidence is given that those composition measurements may be suspect, although pressure, temperature, and density data are accurate. A simplex optimization method was used for the parameters of the model, and the compositions were also treated as adjustable parameters. With this method a much more accurate correlation is obtained, but the optimized compositions differ in two of four cases by more than 3% from the stated compositions.

KEY WORDS: critical region; ethylene; high pressure; mole fraction errors; *n*-butane; simplex optimization; vapor–liquid equilibrium.

1. INTRODUCTION

The Leung–Griffiths model [1], as modified by Moldover, Rainwater, and co-workers [2–4], has successfully correlated high-pressure vapor–liquid equilibria (VLE) of many mixtures. It has also shown promise as a tool for data evaluation, as demonstrated in a case study of carbon dioxide with butane isomers [5] and an experimental and theoretical reexamination of carbon dioxide + propane [6]. In the course of this project, many

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high-quality but unpublished experimental VLE studies, available only in theses, were located. Recently, such investigations of six mixtures [7, 8] were published for the first time, together with highly accurate modified Leung–Griffiths correlations.

In this work we examine the high-pressure VLE data on ethylene + *n*-butane from the unpublished thesis of Williams [9]. The data in their original form are published here for the first time. We report a correlation of this mixture, in which we find that an accurate fit can be obtained only if we shift the mixture compositions from their experimentally stated values.

2. PHASE EQUILIBRIUM DATA

Williams [9] conducted an extensive study up to critical pressures for four fixed compositions of the mixture ethylene + *n*-butane. These data, with permission, are listed in Table I in their original form. They have appeared in cross-plotted form in a VLE compendium; see Ref. 10, p. 518. Cross-plotting, however, can introduce error and is particularly questionable when the experimental compositions are suspect, as we show.

These data were part of a pioneering VLE project at the University of Michigan during 1942–1954 led by Katz [11–14]. That project was important not only for the data produced, but also for the many students who proceeded to lead well-known and prolific phase-equilibrium research groups [15]. From a bibliographic study of high-pressure VLE [4], Williams provides more extensive coverage of the critical region than any other studies, except those from the laboratory of Kay of Ohio State University [7]. In fact, the apparatus by Williams was based on the design of Kay [16].

There is separate evidence that, while the Michigan group accurately measured pressures, temperatures, and densities, their determinations of mixture compositions were inaccurate. Previously, we showed [5] that the data of Poettmann and Katz [12] on carbon dioxide + *n*-butane could be correlated consistently with a large number of more recent studies of that mixture, but only if their experimentally stated compositions were shifted. On a plot of critical temperature versus composition for carbon dioxide + methane, the entries of Donnelly and Katz [11] at methane mole fraction $x = 0.12$ and $x = 0.82$ deviate by about 0.05 from the continuous curve formed by data of other researchers [17–19]. Also, in the paper by Churchill *et al.* [13], mixture compositions are stated as uncertain or not reported.

VLE measurements for ethylene + *n*-butane have also been published by Efremova and Sorina [20]. Their reported data, however, are extensive

Table I. VLE Data of Williams [9] for Ethylene + *n*-Butane

P (MPa)	T (K)	ρ (kg·m^{-3})	P (MPa)	T (K)	ρ (kg·m^{-3})	P (MPa)	T (K)	ρ (kg·m^{-3})
Composition A								
0.3937	302.72	8.82	4.9387	406.54	196.7	5.1118	394.83	350.4
0.5619	315.78	11.85	5.0001	406.07	212.0	5.0918	394.40	347.7
0.6019	318.54	12.51	5.0366	405.72	216.8	4.9649	391.05	363.2
0.8563	332.36	17.26	5.0711	405.38	225.8	4.8387	388.85	371.3
1.1273	343.49	22.31	5.1021	404.94	232.8	4.7622	386.31	378.5
1.5237	356.84	30.79	5.1297	404.60	239.2	4.5388	381.27	393.7
1.5396	357.63	31.37	5.1607	404.03	247.7	4.3789	377.19	404.7
1.7202	362.71	35.26	5.1842	403.72	252.9	4.2003	373.17	415.4
1.8899	367.44	40.03	5.1904	403.43	256.4	3.9907	367.89	427.8
1.9250	368.12	—	5.1890	403.44	257.2	3.7576	362.47	439.2
1.9478	368.09	—	5.2021	403.17	260.5	3.5722	357.43	449.0
1.9491	369.14	42.43	5.2090	402.66	270.7	3.5384	357.08	458.6
2.1932	375.12	49.36	5.2131	402.17	275.2	3.4839	356.63	458.7
2.5042	383.50	61.42	5.2159	401.37	288.1	2.8696	343.88	—
2.7476	386.12	66.03	5.2028	400.54	299.4	2.8565	342.62	—
3.1075	392.16	77.95	5.2007	400.96	294.0	2.8455	343.80	471.2
3.5177	398.26	94.42	5.1986	399.83	—	2.6297	336.78	481.6
3.8445	402.22	110.2	5.1959	399.84	305.6	2.3504	328.25	—
4.3251	405.68	143.7	5.1607	398.84	314.8	2.3353	328.29	494.7
4.5299	406.46	161.9	5.1807	398.26	320.7	2.1801	321.78	504.6
4.6898	406.78	178.2	5.1173	396.64	333.9	1.9374	315.74	513.2
4.8505	406.74	190.5	5.1125	396.16	339.2	1.5231	302.48	530.1
Composition B								
0.4371	297.71	8.85	3.7266	379.36	79.45	6.0963	379.08	—
0.7481	315.16	13.52	4.2030	382.43	—	6.1894	378.28	—
0.7605	318.99	14.91	4.1451	382.44	95.56	6.0805	381.14	—
0.9991	327.07	18.14	4.3699	383.38	103.6	5.9888	382.42	241.2
1.0625	327.72	18.56	4.7098	384.84	—	6.0364	381.85	246.9
1.3603	339.87	24.97	4.7126	384.84	127.9	6.1032	380.77	255.8
1.5017	344.08	27.60	4.8181	384.99	—	6.1170	380.42	259.7
1.9181	354.67	36.02	4.8201	384.97	136.4	6.1315	380.08	261.7
2.4476	363.28	44.90	4.8574	385.39	—	6.1274	380.02	267.5
2.3939	363.46	45.07	4.8574	385.38	140.8	6.1439	379.53	266.7
2.4656	364.68	46.80	5.0056	385.74	155.1	6.1729	378.55	276.5
2.4904	365.10	—	5.4662	385.31	—	6.1812	378.00	275.8
2.5242	365.04	—	5.4462	385.42	198.2	6.1963	377.99	277.6
2.7124	368.26	52.13	5.4662	385.34	—	6.2115	377.45	284.9
2.7345	367.74	—	5.5062	385.47	198.2	6.2480	376.77	289.2
2.9723	371.75	58.27	5.6192	384.93	207.9	6.2570	375.93	294.8
3.6011	378.11	74.91	5.9033	383.27	231.5	6.2522	375.20	300.9

(Continued)

Table I. *(Continued)*

P (MPa)	T (K)	ρ ($kg \cdot m^{-3}$)	P (MPa)	T (K)	ρ ($kg \cdot m^{-3}$)	P (MPa)	T (K)	ρ ($kg \cdot m^{-3}$)
6.2632	374.58	304.2	6.0033	363.57	—	4.3251	333.46	440.1
6.2708	373.28	312.1	5.9033	361.27	370.5	3.7763	324.39	454.8
6.2570	372.21	317.8	5.6771	356.60	386.9	3.4784	318.96	462.2
6.2432	371.21	324.3	5.5854	354.69	—	3.4488	318.49	464.1
6.1377	368.56	334.5	5.4041	351.44	401.6	3.2598	315.10	469.5
6.1577	367.70	342.6	4.9808	343.91	419.7	2.8441	306.50	481.1
6.0570	364.72	356.7	4.7333	339.93	427.7	2.4352	298.81	491.0

Composition C

P (MPa)	T (K)	ρ ($kg \cdot m^{-3}$)	P (MPa)	T (K)	ρ ($kg \cdot m^{-3}$)	P (MPa)	T (K)	ρ ($kg \cdot m^{-3}$)
0.6964	298.59	12.85	5.8261	360.67	133.5	6.7086	349.82	250.8
0.8343	304.26	—	6.1157	360.61	151.4	6.7086	348.84	251.7
0.8343	303.71	—	6.2191	360.48	155.7	6.7120	349.27	254.1
0.8550	304.82	—	6.3983	359.94	161.5	6.7017	348.17	259.8
0.9101	306.59	19.53	6.4432	359.42	176.4	6.6879	347.13	267.2
1.2755	318.59	21.62	6.5500	358.19	189.0	6.6879	346.70	270.3
1.5513	324.47	—	6.6052	356.77	201.1	6.6693	345.43	277.7
1.4962	324.47	25.58	6.6190	356.11	206.3	6.6569	344.66	282.0
1.7306	329.74	29.01	6.6465	354.29	219.7	6.6397	343.50	288.5
1.9650	333.55	32.20	6.6672	354.43	218.5	6.5645	341.82	297.1
2.5028	341.87	40.81	6.6741	354.91	215.2	6.4921	340.08	305.9
2.8475	346.68	46.56	6.6769	353.84	223.8	6.2687	334.43	332.4
2.9785	348.16	49.26	6.6845	353.38	227.3	5.9460	329.11	356.0
3.6287	354.90	64.53	6.6948	352.74	232.8	5.8543	327.30	362.7
4.0610	357.81	77.26	6.7086	349.04	—	5.6206	324.05	374.5
4.6884	359.88	96.88	6.7120	349.28	—	5.0470	315.01	398.9
4.8194	360.13	100.6	6.7120	350.12	—	4.7215	309.74	410.8
5.0194	360.08	—	6.7189	351.13	240.2	4.4064	305.04	421.1
5.3917	360.71	118.7	6.7086	351.38	240.5	3.9686	298.38	434.6
5.5330	360.67	124.1	6.7086	350.88	244.6			

Composition D

P (MPa)	T (K)	ρ ($kg \cdot m^{-3}$)	P (MPa)	T (K)	ρ ($kg \cdot m^{-3}$)	P (MPa)	T (K)	ρ ($kg \cdot m^{-3}$)
0.8846	284.18	13.02	3.7935	329.92	69.95	6.3432	335.46	162.0
0.9115	284.66	—	4.3209	333.49	81.93	6.3887	334.98	170.1
1.0611	288.86	15.38	4.4685	333.91	96.15	6.4342	334.81	172.5
1.4755	299.44	22.90	4.4375	334.42	100.8	6.4887	333.51	181.4
1.6416	302.98	25.16	4.7346	335.50	112.3	6.5121	332.61	186.2
2.1084	311.38	34.87	4.9284	335.98	118.2	6.5307	331.81	190.8
2.3697	315.18	38.71	5.6289	337.28	135.2	6.5004	331.50	195.0
2.8855	321.66	48.27	6.0405	337.11	138.7	6.5411	330.63	200.1
2.8882	320.71	47.43	6.0584	337.09	144.3	6.5521	330.01	204.7
2.9048	323.07	51.62	6.2411	336.31	154.9	6.5604	329.17	211.5
3.1840	324.96	54.88	6.2963	336.11	157.5	6.5604	328.27	217.9

Table I. *(Continued)*

P (MPa)	T (K)	ρ (kg·m^{-3})	P (MPa)	T (K)	ρ (kg·m^{-3})	P (MPa)	T (K)	ρ (kg·m^{-3})
6.5466	327.04	227.1	6.5155	324.92	246.8	5.1090	302.99	362.3
6.5155	326.97	229.6	6.5052	324.62	249.2	4.8732	299.51	374.1
6.5445	326.64	231.4	6.4845	323.59	258.9	4.1182	288.78	391.3
6.5328	326.09	235.9	6.4604	323.06	—	3.8169	284.68	—
6.5293	325.66	—	6.3694	320.66	282.0	3.8107	284.27	—
6.5087	325.44	239.6	6.0364	315.29	314.6	3.7632	284.23	404.3
6.5204	325.36	242.9	5.6675	310.51	332.5	3.7935	283.74	—

interpolations of a much smaller number of measured data points and show certain internal inconsistencies. Their work was not used as input for the present study.

3. NONLINEAR LEUNG–GRIFFITHS OPTIMIZATION

The modified Leung–Griffiths model has been described in detail elsewhere [2–4] and the equations are not repeated here. Unlike traditional equations of state, the model describes critical-region VLE with nonclassical critical exponents. It involves a number of parameters to describe the pure-fluid coexistence curves and the critical locus, as well as a few additional mixture parameters, the number of which depends on the dissimilarity of the two components. Such dissimiliarity is measured by α_{2m}, where

$$\alpha_{2m} = \max(\alpha_2) = \max(\rho_c\, \Delta x/\Delta\rho) \qquad (1)$$

where Δx and $\Delta\rho$ are the vapor–liquid differences in composition and density as the critical locus is approached, and ρ_c is the critical density. Extensive studies [4] have shown that for mixtures such as ethylene + *n*-butane, with $\alpha_{2m} = 0.25$, five mixture parameters suffice to yield an excellent correlation.

Our initial attempt to correlate the data of Williams is shown in Fig. 1. While the dew-bubble curves are smooth and appear to display the proper shape, the correlation of Fig. 1 does not come up to the standards of previous fits of similar mixtures [4–8].

Originally our correlations were performed by visual and graphical methods. More recently, Lynch [21] (and, independently, Sahimi and Taylor [22]) has developed formal nonlinear optimization methods to determine the parameters. Details of the simplex method of Lynch are

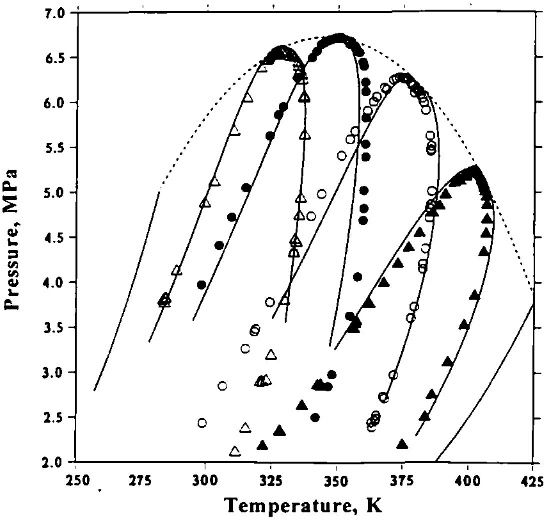

Fig. 1. Phase diagram of ethylene + *n*-butane, bounded on the left by the ethylene vapor pressure curve (solid line), on the top by the critical locus (dashed line), and on the right by the *n*-butane vapor pressure curve (solid line). Experimental data: ▲, composition A (see Table II); ○, B; ●, C; △, D. Solid curves are model dew-bubble curves assuming experimentally stated compositions.

reported elsewhere [21]. The method requires a choice of objective function to be minimized, which Lynch takes to be

$$\sum_i \delta_i^2 = \sum_i \left\{ \left[\frac{T_{\text{ex}} - T_{\text{min}}}{T_{\text{scale}}} \right]^2 + \left[\frac{P_{\text{ex}} - P_{\text{th}}(x_0, T_{\text{min}})}{P_{\text{scale}}} \right]^2 \right\} \tag{2}$$

where the sum is over all data points, x_0 is the composition of the isopleth, subscripts "ex" "th," and "scale" denote experiment, theory, and scale of the P–T diagram (Figs. 1 and 2), and T_{min} is the temperature at which δ_i^2 for a given point is minimized. A similar objective function is constructed for the T–ρ diagram (Fig. 3), and the product of the two objective functions is minimized to obtain the final correlation.

Because of the evidence for errors in composition from the Michigan group as noted in Section 2, in this study we allowed the individual mixture compositions, as well as the mixture parameters of the model, to float as adjustable parameters. Results of the simplex optimization are shown in Figs. 2 and 3. The correlation now achieves the level of agreement of previous fits to other mixtures [2–8]. Model predictions agree with experiment to within 0.03 MPa in pressure, 1 K temperature, and 12 kg · m^{-3} in

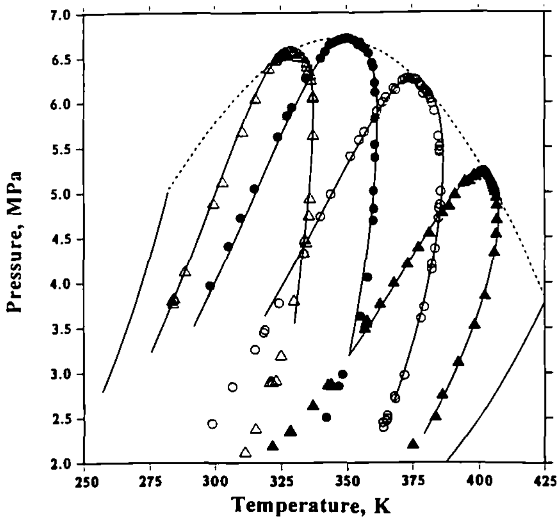

Fig. 2. Same as Fig. 1 except that solid curves are dew-bubble curves from the model based on optimized compositions as listed in Table II.

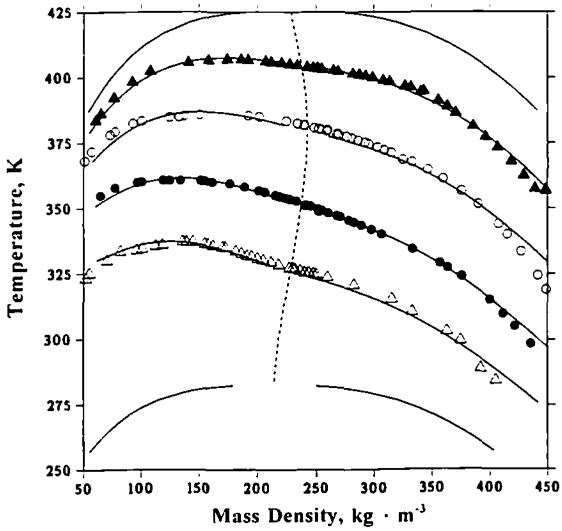

Fig. 3. Temperature–density diagram with optimized coexisting density curves. Symbols same as in Fig. 1: top curve, *n*-butane; bottom curve, ethylene.

Table II. Compositions of Experimental Dew-Bubble Curves

	x (ethylene)	
Label	Experimentally stated	Optimized to model
A	0.1985	0.2324
B	0.4078	0.4460
C	0.6618	0.6564
D	0.8088	0.8052

density. However, our optimized mixture compositions differ from the experimentally stated ones, as shown in Table II. The differences are negligible for the two ethylene-rich mixtures but are substantial for the two *n*-butane-rich ones, 3.4% and 3.8%.

Williams prepared the mixtures by volume in the gaseous, rather than the liquid state; see Ref. 9, p. 10. Determination of mixture composition depended sensitively on second virial coefficients, especially those of *n*-butane at low reduced temperatures, which may not have been accurately known at the time.

4. CONCLUSIONS

Particularly in a study of this nature, care must be taken in judging the theoretical interpretation of experimental data. Our analysis suggests that Williams measured the phase boundary of ethylene + *n*-butane accurately in pressure, temperature, and density, but the compositions determined in Table II by our optimization may be closer to the truth than his stated ones. We would not recommend that his data, with our compositions, be used with the same degree of confidence as data on other mixtures for which all measurements are clearly reliable. Our conclusions must be that Williams' compositions are "suspect," but not necessarily "wrong," although previous case studies [5, 6] have supported similar indications of suspect data from a modified Leung–Griffiths analysis. To clarify the study, it is recommended that ethylene + *n*-butane be remeasured, preferably on isothermal paths as an independent study, and compared against the present correlation.

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