n-Butane–1-Butene–Water System in the Three-Phase Region

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AVAILABLE DATA on systems involving water and mixtures of pure hydrocarbons at elevated temperatures and pressures are scarce. McKetta and Katz (*7, 8*) reported data on the methane-*n*-butane-water system at temperatures from 100° to 280° F. and at pressures from 200 to 3000 p.s.i.a. Villarreal, Bissey, and Nielson (*12*) reported dew point water contents of methane-ethane mixtures at temperatures to 140° F. and pressures to 3000 p.s.i.a.

This research on the *n*-butane-1-butene-water system was undertaken to add to the existing knowledge of phase equilibria in systems involving mixtures of pure hydrocarbons and water at elevated temperatures and pressures.

GENERAL

Figure 1 shows the three binaries made up of three components, *A*, *B*, and *W*. *A* and *B* are miscible in all proportions in the liquid phase. Both *A* and *B* are only partially miscible with *W* in the liquid phase. These three components are similar to those in this investigation where *A* = *n*-butane, *B* = 1-butene, and *W* = water. Pressures indicated in Figure 1 are significant in the *n*-butane-1-butene-water system at 160° F.

The expected ternary diagrams (Figure 2) are useful in showing the approximate areas of the ternary diagram in which to expect single-, two-, or three-phase regions. Present work is in the three-phase region, which exists, generally, at pressures between the three-phase pressures of the *n*-butane-water system and of the 1-butene-water system at any given temperature. At 160° F., this region exists at pressures between 125.4 and 146.5 p.s.i.a.

With respect to the general shape of the phase diagram, the *n*-butane-1-butene-water system differs from the methane-*n*-butane-water system (*7, 8*) principally in that only one of the hydrocarbon components is condensable at the temperatures under consideration in the methane-*n*-butane-water system. This difference causes the three-phase region for the methane-*n*-butane-water system to persist to much higher pressures than in the *n*-butane-1-butene-water system. In the *n*-butane-1-butene-water system, both hydrocarbons are below their critical temperatures, and the three-phase region disappears at the three-phase pressure of the 1-butene-water system at which time the system becomes principally a two-phase hydrocarbon-rich liquid-water-rich liquid system.

Another difference between the *n*-butane-1-butene-water system and the methane-*n*-butane-water system is that the *n*-butane-1-butene-water system involves a paraffin and an olefin of approximately the same molecular weight, making the present work a study in which hydrocarbon molecular weight effects are minimized.

EQUILIBRIUM APPARATUS

A conventional equilibrium apparatus was used. It was essentially a windowed equilibrium cell contained in a constant temperature air bath. The contents of the cell were circulated by a positive displacement, magnetic pump which took vapor from the top of the cell and pumped the vapor into the bottom of the cell. Auxiliary equipment included temperature control and measuring equipment, pressure-measuring equipment, storage reservoirs for the pure compounds, and a high pressure mercury source.

Heise Bourdon tube gages were used to measure pressure inside the cell. The accuracy of the pressure measurements is estimated to be ±2 parts in 1000 parts or ±0.5 p.s.i., whichever is greater.

The temperature of the cell was measured by thermocouples and is estimated to have been measured to within ±0.1° F. at temperatures of 100° and 160° F. and ±0.2° F. at temperatures from 220° to 280° F.

ANALYSES

The contents of the cell were equilibrated for at least 8 hours, although preliminary tests showed that equilibrium

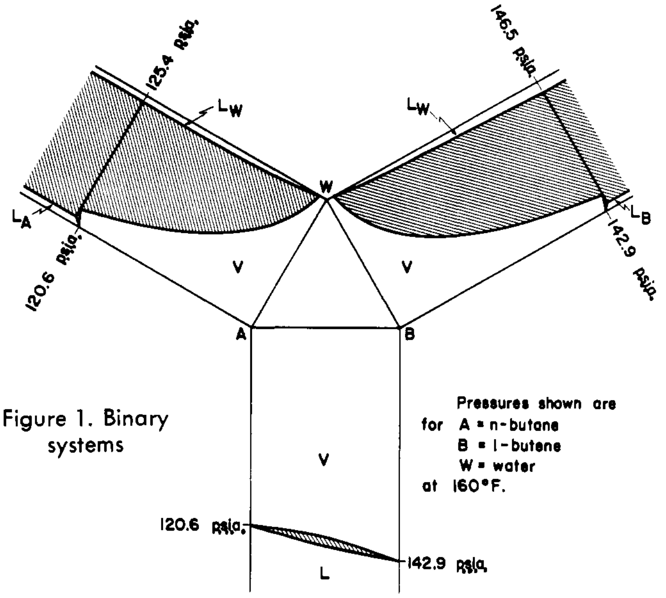

Figure 1. Binary systems

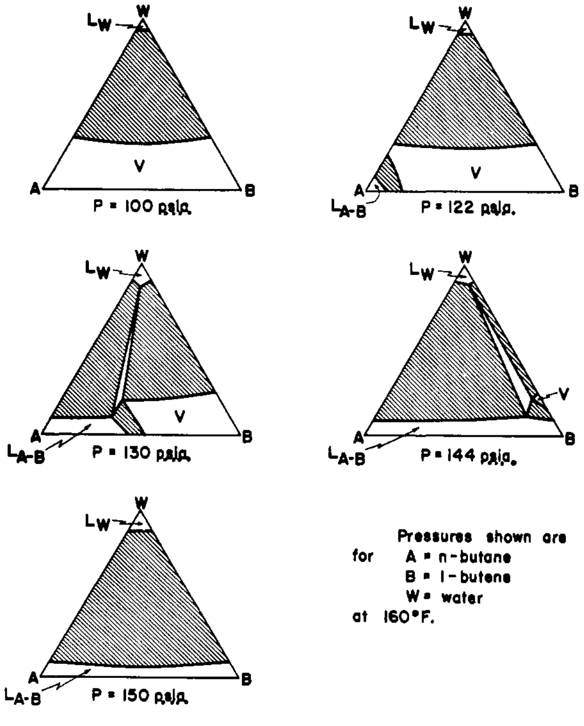

Figure 2. Expected ternary diagrams

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was attained within 1 hour. After settling for an additional hour, samples of each of the three coexisting phases, hydrocarbon-rich liquid, vapor, and water-rich liquid, were withdrawn from the equilibrium cell, while mercury was simultaneously displaced into the cell. The analyses of the three samples can be considered in three general determinations: water content of the hydrocarbon-rich phases, either vapor or liquid; total hydrocarbon content of the water-rich liquid phase; relative amounts of n-butane and 1-butene in each of the three phases.

Water Content of Hydrocarbon-Rich Phases. The water content of the hydrocarbon-rich phases, either vapor or liquid, was determined with an electrolytic hygrometer (Meeco, Hatboro, Pa.) The basic instrument, a commercial model, was modified so that the flow of sample through the instrument was as shown in Figure 3. The output of the electrolytic cell was recorded on a strip chart recorder, the area under the recorded curve being proportional to the total moles of water passing through the electrolytic cell. The total number of sample moles passing through the electrolytic cell were determined by taking P-V-T measurements of the sample. From these two measurements, the mole fraction of water in the original sample from the equilibrium cell was calculated.

It is estimated that the water content of the hydrocarbon-rich liquid phase was determined to within ±4% of the value and that the water content of the vapor phase was determined to within ±4.5% of the value.

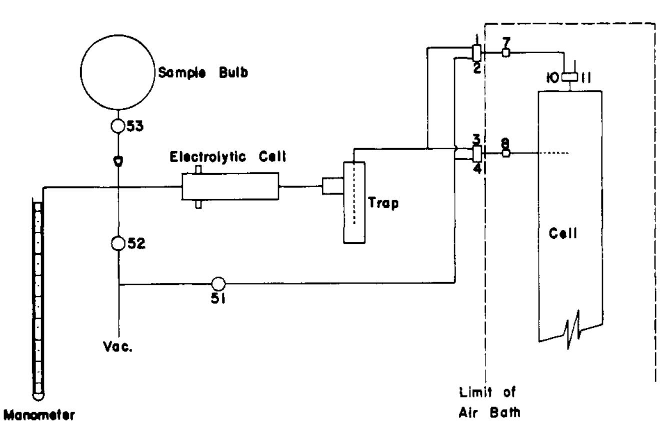

Figure 3. Analytical equipment for hydrocarbon-rich phase

Total Hydrocarbon Content of Water-Rich Liquid. The sample of the water-rich liquid was analyzed by a direct method similar to that used by Kobayashi and Katz (*5*). The detailed analytical procedure is discussed by Wehe (*13, 14*).

Determination of *n*-Butane and 1-Butene. The relative amounts of n-butane and 1-butene in the three gas samples collected from the above analyses were determined by gas chromatography. A Fisher-Gulf partitioner was used employing helium as the carrier gas and a 20-foot long column of ¼-inch copper tubing packed with β, β-oxydipropionitrile on firebrick at 0° C. The chromatograph was calibrated for n-butane, 1-butene, and air before use.

Because the samples existed at low pressures, sometimes as low as 20 mm. of Hg absolute, a low pressure sampling system was used to introduce samples into the instrument. Water in the vapors from the water-rich phase analysis did not interfere with the analysis. It is estimated that the accuracy of the analyses is to about ±0.5 mole %.

MATERIAL USED

Distilled water was boiled under reduced pressure to remove dissolved gases, and the boiling water was immediately charged to the equilibrium apparatus.

n-Butane and 1-butene (Phillips Petroleum Co. research grade hydrocarbons) had a minimum purity of 99.90 mole %. These hydrocarbons were not further purified. Only liquid samples of the hydrocarbons were charged into the equilibrium apparatus.

EXPERIMENTAL RESULTS OF BINARY SYSTEMS

Comparison with Literature. Data for the binary systems, n-butane–water and 1-butene–water, are compared with data reported in the literature in Table I. The agreement is considered very good. Data were taken by the authors on the n-butane–water system at the four temperatures studied and at the three-phase pressures; on the hydrocarbon-rich liquid phase of the 1-butene–water system at the three-phase pressure at four temperatures between 220° and 280° F., the remaining data (Table I) on the 1-butene–water binary being obtained from extrapolated data on the n-butane–1-butene–water ternary system.

Table I. Comparison of Binary Three Phase Data With Literature

Temp., ° F.		Press., P.S.I.A.		Mole Fraction Water × 10^3				Mole Fraction HC in Water-Rich Liq. × 10^5	
				HC-Rich Liq.		Vapor			
Exptl.	Lit.[a]	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
				n-Butane–Water System[a]					
100.2	100	52.2	52.45	0.91	0.5	14.3	16.7	4.37	6.2
99.9		52.1		0.83		15.7		4.84	
159.9	160	124.9	125.4	3.38	2.1	35.1	33.8	5.89	8.7
220.2	220	260.1	259.3	10.0	8.5	55.6	54.1	. . .	14.0
220.3		260.9		9.25		53.0		10.5	
280.0	280	491.6	490.9	28.0	26.8	75.1	70.8	18.6	22.0
280.0		491.5		27.8		74.6		21.5	
				1-Butene–Water System					
100	100	63.0[b]	63.2[c]	1.61[b]	1.41[d] 1.75[f]	11.0[b]	13[e]	21.84[b]	21.7[c] 22.8[f]
160	160	146.9[b]	146.5[c]	5.73[b]	3.72[d] 5.71[f]	26.0[b]	29[e]	26.16[b]	24.2[c] 26.7[f]
219.9	220	300.1	301[c]	15.9	10.83[d]	. . .	50[e]	. . .	36.4[c]
220		300.2[b]		15.8[b]	15.5[f]	50.3[b]		39.38[b]	34.9[f]
240.2	. . .	372.0	. . .	22.6	. . .	. . .	. . .	. . .	. . .
260.2	. . .	457.0	. . .	31.9	. . .	. . .	. . .	. . .	. . .
280.1	280	. . .	561[c]	42.8	32.14[d]	. . .	68[e]	. . .	61.5[c]
280.1		558.6		. . .	33.7[f]				55.8[f]
280		558.4[b]		42.5[b]		68.6[b]		64.71[b]	. . .

[a] Literature data refer to (*9, 10*).
[b] Extrapolated data.
[c] Brooks and McKetta (*4*).
[d] Brooks and McKetta (*3*).
[e] Brooks, Haughn, and McKetta (*2*).
[f] Leland, McKetta, and Kobe (*6*).

EXPERIMENTAL RESULTS OF THE TERNARY SYSTEM

The experimental results are given in Table II and the smoothed data are given in Table III. The results are presented graphically in Figures 4 to 8.

n-Butane–1-Butene Equilibria. The n-butane–1-butene equilibria are shown on a dry basis in Figure 4 as $(y - x')$ versus x' where y is the mole fraction of one of the hydrocarbons in the vapor (dry basis) and x' is the mole fraction of the same hydrocarbon in the hydrocarbon-rich liquid phase (dry basis).

A pressure-composition plot is generally what would be expected for the n-butane–1-butene–water system. Since the hydrocarbon-water system is essentially immiscible, the total pressure at the lower temperatures, 100° and 160° F., is the sum of the vapor pressure of the hydrocarbon, either pure or in a mixture, and the vapor pressure of water. At 220° and 280° F., the total pressure is greater than the sum of the vapor pressures, the differences between the two pressures being termed a three-phase residual pressure. This residual pressure varies with composition of the hydrocarbon and temperature (Table IV). These three-phase residual pressures are of the same magnitude as those found by Reamer and others (*9*) for the n-butane–water system and by Brooks (*1*) for the 1-butene–water system.

The $(y - x')$ *vs.* x' data for the n-butane–1-butene–water system on a dry basis are essentially the same as those obtained by Sage and Lacey (*11*) for the n-butane–1-butene system at all temperatures except 100° F. where $(y - x')$ for the n-butane–1-butene–water system is slightly greater.

Water Content of Hydrocarbon Vapor. The data on the water content of the hydrocarbon vapor are shown in Figure 5. Generally, water content at the three-phase pressure decreases as the concentration of 1-butene in the vapor increase and the three-phase pressure increases. The data are not of sufficient precision to make differentiation possible between the effect of increased pressure and the effect of increased concentration of 1-butene in the vapor on the dew point composition of water in the vapor. The entire pressure range for an isotherm is very small.

Although the curve in Figure 5 at 280° F. was drawn with a minimum, it could have been drawn as a straight line and remain within the observed dispersion of the data.

Hydrocarbon Content of Water-Rich Liquid. Data on solubility of the individual hydrocarbons in the water-rich liquid phase were taken at constant temperature and at pressures varying from the three-phase pressure of the n-butane–water system to that of the 1-butene–water system. These data are plotted in Figure 6, which is an expanded apex of a triangular diagram. This pressure range is small at all temperatures studied, so that its effect on the fugacity coefficient of the hydrocarbons can be neglected. A thermodynamic analysis of these data is as follows:

If the vapors can be assumed to form an ideal solution, then the Lewis and Randall rule, Equation 1, holds.

$$(f_2)_V = y_2(f_2^0) \tag{1}$$

(Text continued on page 172)

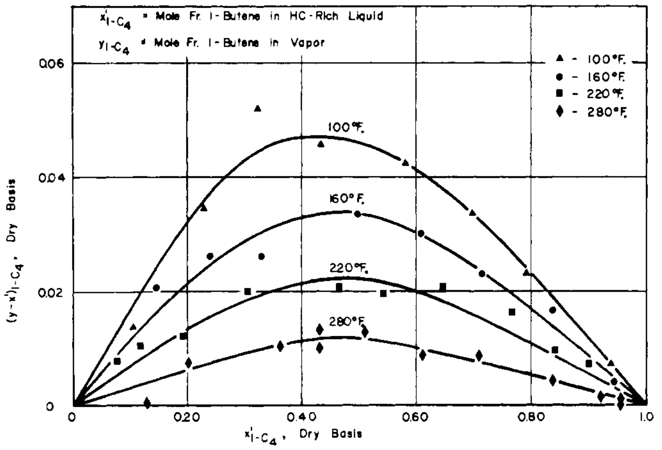

Figure 4. $(y - x')_{1-C_4}$ vs. x'_{1-C_4}, dry basis, for ternary

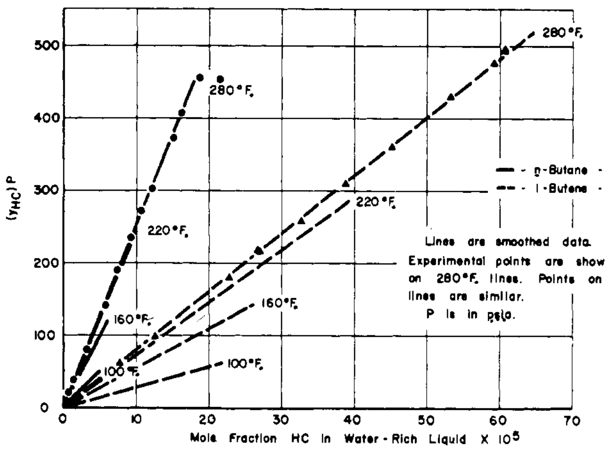

Figure 7. (y_{HC}) P vs. x''_{HC} at three-phase pressure for ternary

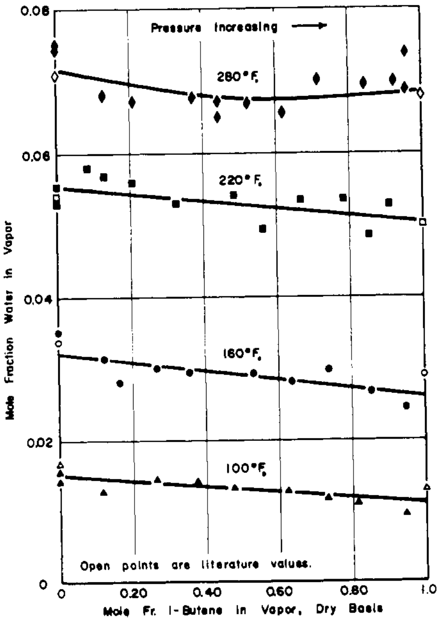

Figure 5. Water content of vapor for ternary

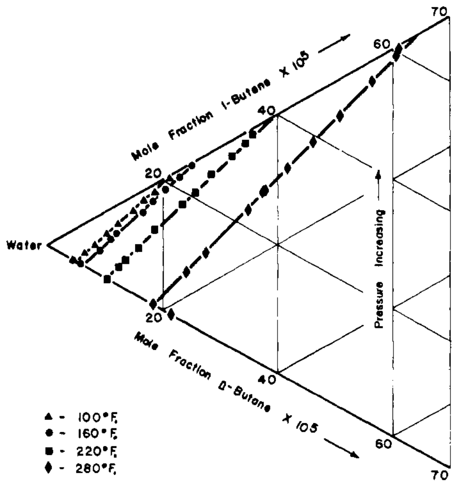

Figure 6. Solubility of hydrocarbons in the water-rich liquid for ternary

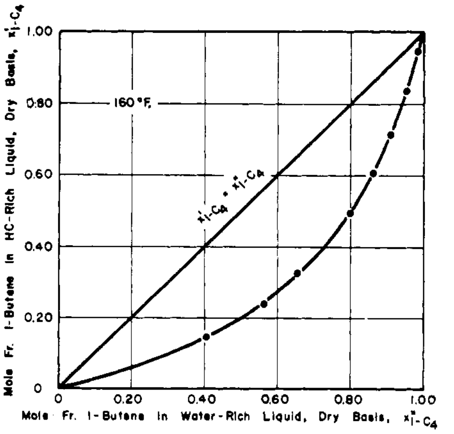

Figure 8. Distribution of 1-butene between liquid phases

Table II. Experimenal Data for *n*-Butane–1-Butene–Water System

Run No.	Temp., ° F.	P., P.S.I.A.	Analyses, Mole Fraction, Dry Basis				Analyses, Mole Fraction, Wet Basis								
			HC liquid		HC vapor		Water in HC		HC in Water × 10^5			HC Liquid		HC Vapor	
			Butane	Butene	Butane	Butene	Liq. × 10^3	Vapor	Butane	Butene	Total	Butane	Butene	Butane	Butene
90	100.2	52.2	1.000	. . .	1.000	. . .	0.91	0.0143	4.37	. . .	4.37	0.99909	. . .	0.9857	. . .
91	159.9	124.9	1.000	. . .	1.000	. . .	3.38	0.0351	5.89	. . .	5.89	0.99662	. . .	0.9649	. . .
92	220.2	260.1	1.000	. . .	1.000	. . .	10.0	0.0556	. . .	. . .	. . .	0.99000	. . .	0.9444	. . .
93	280.0	491.6	1.000	. . .	1.000	. . .	28.0	0.0751	18.6	. . .	18.6	0.97196	. . .	0.9249	. . .
94	280.0	491.5	1.000	. . .	1.000	. . .	27.8	0.0746	21.5	. . .	21.5	0.97225	. . .	0.9254	. . .
95	220.3	260.9	1.000	. . .	1.000	. . .	9.3	0.0530	10.5	. . .	10.5	0.99075	. . .	0.9470	. . .
96							Reported in Table I								
97							Reported in Table I								
98	99.9	52.1	1.000	. . .	1.000	. . .	0.83	0.0157	4.84	. . .	4.84	0.99917	. . .	0.9843	. . .
99	99.9	56.0	0.6756	0.3244	0.6237	0.3763	1.02	0.0143	3.35	7.05	10.40	0.6749	0.3241	0.6148	0.3709
100	99.9	54.8	0.7714	0.2286	0.7368	0.2632	0.88	0.0146	4.15	4.15	8.30	0.7707	0.2284	0.7260	0.2594
101	99.9	53.1	0.8955	0.1045	0.8817	0.1183	0.74	0.0128	4.61	2.01	6.62	0.8949	0.1044	0.8704	0.1168
102	99.9	57.1	0.5670	0.4330	0.5213	0.4787	1.10	0.0134	2.98	9.39	12.37	0.5664	0.4325	0.5143	0.4723
103	100.0	58.7	0.4205	0.5795	0.3780	0.6220	1.22	0.0128	2.25	12.69	14.94	0.4200	0.5788	0.3732	0.6140
104	99.9	59.8	0.3028	0.6972	0.2691	0.7309	1.29	0.0117	1.69	15.13	16.82	0.3024	0.6963	0.2660	0.7223
105	99.9	60.8	0.2079	0.7921	0.1846	0.8154	1.43	0.0111	1.18	17.36	18.54	0.2076	0.7910	0.1825	0.8064
106	99.9	62.2	0.0610	0.9390	0.0537	0.9463	1.62	0.0094	0.36	20.86	21.22	0.0609	0.9375	0.0532	0.9374
107	160.1	146.0	0.0558	0.9442	0.0517	0.9483	5.96	0.0244	0.42	24.87	25.29	0.0555	0.9385	0.0504	0.9252
108	160.1	144.0	0.1634	0.8366	0.1467	0.8533	5.30	0.0267	1.06	21.95	23.01	0.1625	0.8322	0.1428	0.8305
109	160.1	141.8	0.2850	0.7150	0.2619	0.7381	4.85	0.0298	1.86	18.76	20.62	0.2836	0.7116	0.2541	0.7161
110	160.1	139.2	0.3924	0.6076	0.3622	0.6378	4.49	0.0282	2.53	15.93	18.46	0.3906	0.6049	0.3520	0.6198
111	160.3	137.1	0.5029	0.4971	0.4693	0.5307	4.25	0.0293	3.29	13.16	16.45	0.5008	0.4949	0.4556	0.5151
112	160.1	133.1	0.6711	0.3289	0.6449	0.3551	3.98	0.0295	4.16	7.88	12.04	0.6684	0.3276	0.6259	0.3446
113	160.1	131.0	0.7597	0.2403	0.7334	0.2666	3.56	0.0301	4.80	6.25	11.05	0.7570	0.2394	0.7113	0.2586
114	160.1	128.9	0.8545	0.1455	0.8337	0.1663	3.30	0.0281	5.43	3.70	9.13	0.8517	0.1450	0.8103	0.1616
115	160.1	127.8	. . .	. . .	0.8766	0.1234	. . .	0.0314	. . .	. . .	. . .	. . .	. . .	0.8491	0.1195
116	220.0	262.2	0.9222	0.0778	0.9143	0.0857	10.6	0.0580	9.69	2.94	12.63	0.9124	0.0770	0.8613	0.0807
117	220.0	264.2	0.8820	0.1180	0.8715	0.1285	10.4	0.0569	9.12	4.56	13.68	0.8728	0.1168	0.8219	0.1212
118	220.0	267.4	0.8072	0.1928	0.7950	0.2050	11.1	0.0560	8.52	7.43	15.95	0.7982	0.1907	0.7505	0.1935
119	219.9	272.6	0.6938	0.3062	0.6737	0.3263	11.6	0.0531	7.04	11.81	18.85	0.6858	0.3026	0.6379	0.3090
120	220.0	279.2	0.5353	0.4647	0.5144	0.4856	12.5	0.0542	5.51	18.01	23.52	0.5286	0.4589	0.4865	0.4593
121	220.0	282.2	0.4584	0.5416	0.4387	0.5613	13.0	0.0495	4.72	20.90	25.62	0.4525	0.5345	0.4170	0.5335
122	220.0	286.3	0.3541	0.6459	0.3332	0.6668	13.6	0.0535	3.65	25.07	28.72	0.3493	0.6371	0.3154	0.6311
123	220.0	291.1	0.2328	0.7672	0.2164	0.7836	14.5	0.0536	2.41	29.79	32.20	0.2294	0.7561	0.2048	0.7416
124	219.9	293.6	0.1592	0.8408	0.1495	0.8505	14.9	0.0485	1.73	32.85	34.58	0.1568	0.8283	0.1422	0.8093
125	220.0	295.9	0.0981	0.9019	0.0908	0.9092	15.4	0.0528	1.03	34.71	35.74	0.0966	0.8880	0.0860	0.8612
126	279.8	554.3	0.0430	0.9570	0.0419	0.9581	42.1	0.0737	0.72	60.93	61.65	0.0412	0.9167	0.0388	0.8875
127	279.9	554.8	0.0436	0.9564	0.0436	0.9564	42.0	0.0686	0.77	60.70	61.47	0.0418	0.9162	0.0406	0.8908
128	279.9	553.6	0.0778	0.9222	0.0764	0.9236	41.6	0.0699	1.40	59.21	60.61	0.0746	0.8838	0.0711	0.8590
129	280.0	548.9	0.1616	0.8384	0.1571	0.8429	39.7	0.0696	3.23	53.28	56.51	0.1552	0.8051	0.1462	0.7842
130	279.9	540.5	0.2907	0.7093	0.2821	0.7179	37.9	0.0702	5.77	45.19	50.96	0.2797	0.6824	0.2623	0.6675
131	279.9	534.2	0.3890	0.6110	0.3803	0.6197	36.7	0.0656	7.43	38.85	46.28	0.3747	0.5886	0.3553	0.5791
132	279.9	528.0	0.4903	0.5097	0.4774	0.5226	35.5	0.0669	9.15	32.70	41.85	0.4729	0.4916	0.4455	0.4876
133	279.9	522.9	0.5688	0.4312	0.5555	0.4445	34.6	0.0651	10.80	26.93	37.73	0.5491	0.4163	0.5193	0.4156
134	280.0	522.6	0.5693	0.4307	0.5593	0.4407	34.3	0.0672	10.76	27.19	37.95	0.5498	0.4159	0.5217	0.4111
135	280.0	518.1	0.6375	0.3625	0.6271	0.3729	33.8	0.0677	12.19	22.84	35.03	0.6160	0.3502	0.5846	0.3477
136	280.0	506.4	0.7979	0.2021	0.7904	0.2096	31.7	0.0672	15.10	12.58	27.68	0.7726	0.1957	0.7373	0.1955
137	279.9	501.0	0.8715	0.1285	0.8710	0.1290	31.0	0.0681	16.29	7.86	24.15	0.8445	0.1245	0.8117	0.1202
138	280.1	. . .	0.0008	0.9992	. . .	. . .	42.8	. . .	. . .	. . .	. . .	0.0008	0.9564	. . .	. . .
139	219.9	300.1	0.0008	0.9992	. . .	. . .	15.9	. . .	. . .	. . .	. . .	0.0008	0.9833	. . .	. . .
140	240.2	372.0	0.0008	0.9992	. . .	. . .	22.6	. . .	. . .	. . .	. . .	0.0008	0.9766	. . .	. . .
141	260.2	457.0	0.0008	0.9992	. . .	. . .	31.9	. . .	. . .	. . .	. . .	0.0008	0.9673	. . .	. . .
142	280.1	558.6	0.0008	0.9992	. . .	. . .	. . .	. . .	. . .	. . .	. . .	0.0008	. . .	. . .	. . .

Table III. Smoothed Data for *n*-Butane–1-Butene–Water System

		Analyses, Mole Fraction, Dry Basis				Analyses, Mole Fraction, Wet Basis								
Temp., °F.	P., P.S.I.A.	HC Liquid		HC Vapor		Water in HC		HC in Water × 10^5			HC Liquid		HC Vapor	
		Butane	Butene	Butane	Butene	Liq. × 10^3	Vapor	Butane	Butene	Total	Butane	Butene	Butane	Butene
100.0	52.2	1.0000	0	1.0000	0	0.62	0.0151	5.11	0	5.11	0.9994	0	0.9849	0
100.0	53.3	0.9000	0.1000	0.8830	0.1170	0.72	0.0147	4.61	2.20	6.81	0.8994	0.0999	0.8700	0.1153
100.0	54.5	0.8000	0.2000	0.7678	0.2322	0.82	0.0143	4.10	4.40	8.50	0.7993	0.1999	0.7568	0.2289
100.0	55.6	0.7000	0.3000	0.6570	0.3430	0.93	0.0138	3.60	6.62	10.22	0.6993	0.2998	0.6479	0.3383
100.0	56.8	0.6000	0.4000	0.5531	0.4469	1.03	0.0134	3.09	8.81	11.90	0.5994	0.3996	0.5457	0.4409
100.0	57.9	0.5000	0.5000	0.4540	0.5460	1.14	0.0130	2.59	10.98	13.57	0.4994	0.4995	0.4481	0.5389
100.0	58.9	0.4000	0.6000	0.3588	0.6412	1.25	0.0126	2.08	13.10	15.18	0.3995	0.5992	0.3543	0.6331
100.0	60.0	0.3000	0.7000	0.2668	0.7332	1.33	0.0122	1.59	15.28	16.87	0.2996	0.6991	0.2635	0.7243
100.0	61.0	0.2000	0.8000	0.1769	0.8231	1.43	0.0118	1.07	17.43	18.50	0.1997	0.7989	0.1748	0.8134
100.0	62.0	0.1000	0.9000	0.0884	0.9116	1.52	0.0114	0.58	19.60	20.18	0.0998	0.8987	0.0874	0.9012
100.0	63.0	0	1.0000	0	1.0000	1.61	0.0110	0	21.84	21.84	0	0.9984	0	0.9890
160.0	125.3	1.0000	0	1.0000	0	2.86	0.0321	6.20	0	6.20	0.9971	0	0.9679	0
160.0	127.6	0.9000	0.1000	0.8883	0.1117	3.17	0.0314	5.60	2.59	8.19	0.8971	0.0997	0.8604	0.1082
160.0	130.0	0.8000	0.2000	0.7783	0.2217	3.46	0.0307	5.01	5.18	10.19	0.7972	0.1993	0.7544	0.2149
160.0	132.3	0.7000	0.3000	0.6711	0.3289	3.75	0.0300	4.41	7.80	12.21	0.6974	0.2988	0.6510	0.3190
160.0	134.5	0.6000	0.4000	0.5669	0.4331	4.03	0.0294	3.79	10.42	14.21	0.5976	0.3984	0.5502	0.4204
160.0	136.7	0.5000	0.5000	0.4663	0.5337	4.31	0.0288	3.18	13.06	16.24	0.4978	0.4979	0.4529	0.5183
160.0	138.9	0.4000	0.6000	0.3697	0.6303	4.60	0.0282	2.55	15.68	18.23	0.3982	0.5972	0.3593	0.6125
160.0	141.0	0.3000	0.7000	0.2757	0.7243	4.89	0.0276	1.94	18.24	20.18	0.2985	0.6966	0.2681	0.7043
160.0	143.1	0.2000	0.8000	0.1831	0.8169	5.17	0.0271	1.31	20.87	22.18	0.1990	0.7958	0.1781	0.7948
160.0	144.6	0.1000	0.9000	0.0913	0.9087	5.46	0.0266	0.68	23.40	24.08	0.0995	0.8950	0.0889	0.8845
160.0	146.9	0	1.0000	0	1.0000	5.73	0.0260	0	26.16	26.16	0	0.9943	0	0.9740
220.0	259.3	1.0000	0	1.0000	0	9.60	0.0555	10.21	0	10.21	0.9904	0	0.9445	0
220.0	263.7	0.9000	0.1000	0.8928	0.1072	10.2	0.0549	9.29	3.72	13.01	0.8908	0.0990	0.8438	0.1013
220.0	268.0	0.8000	0.2000	0.7863	0.2137	10.9	0.0544	8.32	7.49	15.81	0.7913	0.1978	0.7435	0.2021
220.0	272.2	0.7000	0.3000	0.6815	0.3185	11.5	0.0538	7.32	11.31	18.63	0.6920	0.2965	0.6448	0.3014
220.0	276.4	0.6000	0.4000	0.5786	0.4214	12.1	0.0533	6.31	15.23	21.54	0.5927	0.3952	0.5478	0.3989
220.0	280.4	0.5000	0.5000	0.4777	0.5223	12.7	0.0527	5.31	19.17	24.48	0.4936	0.4937	0.4525	0.4948
220.0	284.5	0.4000	0.6000	0.3800	0.6200	13.4	0.0523	4.30	23.11	27.41	0.3947	0.5919	0.3601	0.5876
220.0	288.5	0.3000	0.7000	0.2842	0.7158	14.0	0.0518	3.28	27.07	30.35	0.2958	0.6902	0.2695	0.6787
220.0	292.5	0.2000	0.8000	0.1892	0.8108	14.6	0.0513	2.22	31.10	33.32	0.1971	0.7883	0.1795	0.7692
220.0	296.4	0.1000	0.9000	0.0946	0.9054	15.2	0.0508	1.16	35.19	36.35	0.0985	0.8863	0.0898	0.8594
220.0	300.2	0	1.0000	0	1.0000	15.8	0.0503	0	39.38	39.38	0	0.9842	0	0.9497
280.0	491.3	1.0000	0	1.0000	0	28.4	0.0718	18.32	0	18.32	0.9716	0	0.9282	0
280.0	498.9	0.9000	0.1000	0.8968	0.1032	29.7	0.0707	16.68	5.95	22.63	0.8733	0.0970	0.8334	0.0959
280.0	506.3	0.8000	0.2000	0.7937	0.2063	31.0	0.0696	15.00	12.11	27.11	0.7752	0.1938	0.7385	0.1919
280.0	513.6	0.7000	0.3000	0.6907	0.3093	32.4	0.0687	13.22	18.45	31.67	0.6773	0.2903	0.6432	0.2881
280.0	520.7	0.6000	0.4000	0.5885	0.4115	33.8	0.0680	11.41	24.89	36.30	0.5797	0.3865	0.5485	0.3835
280.0	527.5	0.5000	0.5000	0.4882	0.5118	35.3	0.0676	9.60	31.35	40.95	0.4824	0.4823	0.4552	0.4772
280.0	534.0	0.4000	0.6000	0.3899	0.6101	36.7	0.0675	7.72	37.84	45.56	0.3853	0.5780	0.3636	0.5689
280.0	540.4	0.3000	0.7000	0.2922	0.7078	38.2	0.0675	5.85	44.44	50.29	0.2886	0.6732	0.2725	0.6600
280.0	546.5	0.2000	0.8000	0.1947	0.8053	39.6	0.0677	3.94	51.11	55.05	0.1921	0.7683	0.1815	0.7508
280.0	552.5	0.1000	0.9000	0.0974	0.9026	41.0	0.0681	1.99	57.82	59.81	0.0959	0.8631	0.0908	0.8411
280.0	558.4	0	1.0000	0	1.0000	42.5	0.0686	0	64.71	64.71	0	0.9575	0	0.9314

From the definition of the fugacity coefficient

$$(f_2^0)_V = \nu_{P,T} P \qquad (2)$$

Then

$$(f_2)_V = y_2 \nu_{P,T} P \qquad (3)$$

Henry's law, written in terms of fugacities, is

$$(f_2)_V = k x_2'' \qquad (4)$$

If Equation 4 holds, then:

$$y_2 \nu_{P,T} P = k x_2'' \qquad (5)$$

Since T is constant and the effect of P on $\nu_{P,T}$ is considered negligible (see above), then $\nu_{P,T}$ is constant, or

$$y_2 P = k' x_2'' \qquad (6)$$

where

$$k' = \frac{k}{\nu_{P,T}} \qquad (7)$$

Thus, if Equation 4 holds, a plot of y_2P *vs.* x_2 should produce a straight line. This plot is shown in Figure 7 at the four temperatures studied for each of the two hydrocarbons in water. Straight lines were obtained, showing that Equation 4 holds under the conditions of this investigation.

The above analysis can be considered to be a method of testing Henry's law, written in terms of fugacity, or to be a good means of predicting ternary solubility data from binary data at the same temperature and pressure conditions.

As a means of testing Henry's law written in terms of fugacity, it provides a test in regions where fugacity coefficients for pure solute vapors are not available—i.e., at pressures above the vapor pressure of the pure solute.

Wiebe and Gaddy (*15*) have compared calculated values with experimental solubilities of mixtures of hydrogen and nitrogen in water at 25° C. at pressures from 50 to 1000 atm. Although they did not present the above thermodynamic analysis, it can be shown that their method of calculation can be derived from the above thermodynamic analysis, if it is assumed that the dew point water content of the vapor is independent of the nature of the gas. Thus, Wiebe and Gaddy (*15*) also note that the above method is reasonably good for predicting solubilities of mixtures of gases in water from solubilities of the pure gases in water.

Water Content of Hydrocarbon-Rich Liquid. A plot of the water content of the hydrocarbon-rich liquid *vs.* the mole fraction of 1-butene in the hydrocarbon-rich liquid (dry basis) shows that the water content of the three-phase hydrocarbon-rich liquid increases almost linearly as the mole fraction of 1-butene in the hydrocarbon-rich liquid and the three-phase pressure increase.

Since there is only a small effect of pressure on the solubility of water in hydrocarbon and the pressure change is only slight at a given temperature, the effect shown is such a plot at each temperature is a result of changing the solvent from *n*-butane to 1-butene, the solute (water) remaining the same. This is different from the hydrocarbon content of the water-rich liquid, where the solvent is water and the solute is changed from *n*-butane to 1-butene.

Distribution of 1-Butene between Liquid Phases. Figure 8 is a plot of the mole fraction of 1-butene in the hydrocarbon-rich liquid *vs.* the mole fraction of 1-butene in the water-rich liquid at 160° F., both on a water-free basis. The compositions are taken at the three-phase pressures, and therefore pressure is not constant in this figure. The data at 100°, 220°, and 280° F. are similar to those at 160° F.

Figure 8 shows that water is selective for 1-butene when in equilibrium with *n*-butane–1-butene mixtures at the three-phase conditions. The solubility of the hydrocarbons in water at these conditions is, however, small, a factor which must be considered in attempting to use water as an extractive agent for 1-butene.

Table IV. Residual Pressures

Temp., ° F.	Mole Fraction 1-Butene in HC-Rich Liquid, Dry Basis	Residual Pressure, P.S.I.
220	0	0.9
220	0.4	1.5 max. value
220	1.0	0.4
280	0	6.1
280	0.4	7.5 max. value
280	1.0	3.2

A graph of the mole fraction of 1-butene in the vapor *vs.* the mole fraction of 1-butene in the water-rich liquid at the three-phase conditions, both on a water-free basis, would be similar to Figure 8 because the equilibrium compositions of the hydrocarbon-rich liquid and vapor are close to each other.

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NOMENCLATURE

f = fugacity
f^0 = fugacity of a pure component at the temperature and pressure of the solution
k, k' = constants
P = total pressure
T = absolute temperature
x' = mole fraction in hydrocarbon-rich liquid phase
x'' = mole fraction in water-rich liquid phase
y = mole fraction in vapor phase
ν = fugacity coefficient

Subscripts

A = component A
B = component B
P = pressure
T = temperature
V = vapor phase
W = component W or water
1 = component 1
2 = component 2

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