Vapor-Liquid Equilibrium in the Propylene-Water System

C. C. Li[1] and JOHN J. McKETTA
The University of Texas, Austin, Texas

Experimental data are presented covering the mutual solubilities of propylene in water in (a) the 2-phase region of vapor and water-rich liquid, (b) the 2-phase region of propylene-rich liquid and water-rich liquid, and (c) the 3-phase region of the vapor, propylene-rich liquid and water-rich liquid. The experimental temperatures range from 100° to 280° F., while the pressure range is from 36.2 to 4794.7 p.s.i.a.

THE KNOWLEDGE of the behavior of systems involving hydrocarbons and water, especially at high pressure and temperature, is of considerable importance in petrochemical, refining, and producing industries. The purpose of this study is to contribute to the knowledge of the phase behavior of the propylene-water binary system. The experimental work of this investigation covers the mutual solubilities of propylene and water in the two-phase region of vapor and water-rich liquid, the two-phase region of propylene-rich liquid and water-rich liquid, and the three-phase region of vapor, propylene-rich liquid, and water-rich liquid. The experimental temperatures range from 100° to 280° F. while the pressure range is from 36.2 to 4794.7 p.s.i.a.

The experimental data are presented as total pressure-composition diagrams, at a constant temperature, throughout the investigation except in the three-phase region. The three-phase data are plotted as temperature vs. composition since here the temperature and pressure are uniquely defined in a binary system.

[1] Present address, Allied Chemical Co., Morristown, N. J.

Table I. Experimental data in the two-phase vapor-liquid region

Temp., ° F.	Pressure, P.S.I.A.	Water-Rich Liquid Mole Fraction of Propylene × 10^4	Propylene-Rich Vapor Mole Fraction of Water × 10^4	Temp., ° F.	Pressure, P.S.I.A.	Water-Rich Liquid Mole Fraction of Propylene × 10^4	Propylene-Rich Vapor Mole Fraction of Water × 10^4
100.05	37.0	1.5236	269.6	220,20	1534.0	13.2022	111.3
100.10	66.3	2.9767	126.1	220.20	1832.2	13.5276	97.1
100.00	93.0	4.1805	90.0	220.25	2037.7	13.7631	...
100.05	130.0	5.5750	63.9	220.20	2123.0	...	89.8
100.10	167.7	7.0699	46.5	220.20	2450.0	14.2283	84.7
100.10	205.0	7.6421	39.2	220.20	3046.0	14.9856	84.3
100.00	215.6	7.9896	36.5	220.25	3708.0	15.5092	81.4
160.25	77.2	2.0360	619.2	220.25	4283.5	16.0112	77.3
160.20	136.6	4.2861	344.9	220.30	4701.0	...	78.0
160.25	187.0	5.5390	234.6	280.02	209.3	...	2585.8
160.20	219.0	5.3539	183.7	280.02	229.2	4.6776	...
160.25	289.5	6.9974	139.9	280.02	309.5	6.0831	1809.5
160.25	328.0	8.1204	125.5	280.05	408.0	8.0909	1186.8
160.00	370.5	8.4676	104.0	280.05	507.0	9.5986	968.6
160.25	432.0	9.1853	96.4	279.92	596.0	12.4658	785.4
220.10	117.1	1.9709	1629.3	280.02	710.0	...	692.5
220.05	183.1	3.0152	926.0	280.02	848.0	13.9960	554.4
220.20	247.0	4.9579	757.4	279.85	1123.0	16.3154	446.1
220.20	344.8	6.2384	510.0	279.85	1324.0	17.1891	356.1
220.20	393.5	6.8842	440.9	279.85	1489.0	17.1560	341.7
220.20	488.0	8.4674	328.8	279.85	1910.0	18.1504	276.6
220.20	586.0	9.7630	283.8	279.85	2210.0	18.7990	278.4
220.30	693.5	11.1659	248.1	279.85	2813.0	19.5650	253.0
220.20	816.0	12.1382	192.1	279.85	3274.0	20.3464	248.6
220.20	1038.5	12.8830	161.6	279.85	3755.0	21.0183	234.3
220.25	1252.5	13.3389	131.6	279.85	4670.0	22.6356	207.3

EXPERIMENTAL

Apparatus. The apparatus was essentially the same as described in detail by Wehe and McKetta (*7, 8*). Only a few minor changes were made to adapt the equipment to this system. The apparatus consisted of a high pressure windowed equilibrium cell which is enclosed within an insulated constant temperature air bath, charging lines to admit the propylene and water, and separate sampling lines for removing portions of the equilibrium phases.

Portions of the lightest phase were taken from the top of the equilibrium cell and pumped into the bottom of the cell using a positive displacement magnetic pump. Auxiliary equipment included temperature and pressure controls, and storage reservoirs for the propylene, water and mercury.

The pressure was measured using two Heise Bourdon tube gages (a 0 to 600 p.s.i. range and a 0 to 5000 p.s.i. range). At the start and at the end of each isotherm the gages were calibrated against an Aminco dead weight gage.

The analytical equipment for the propylene-rich phases consisted of a modified electrolytic water analyzer (Model W, Manufacturing Equipment and Engineering Co.), a Honeywell Type 153 Electronik recorder with a range of 0 to 50 mv. and a continuous integrator. The entire apparatus was calibrated before and after the experimental work using known samples. The analytical apparatus for the water-rich phase was discussed in detail by Wehe and McKetta (*9*).

MATERIALS

The propylene used in this work was obtained from Phillips Petroleum Co. A chromatographic analysis of the liquid portion of the cylinders averaged 99.65% propylene and 0.35% propane. The water was taken from the departmental distilled water supply. To remove dissolved gases, the water was heated to boiling under reduced pressure and charged to the equilibrium cell immediately. No trace of Cl^- or Ca^{--} ions was detected in the water.

RESULTS

The experimental results on the compositions of the equilibrium phases are shown in Table I, II, and III.

Table II. Experimental Data in the Two-Phase Liquid-Liquid Region

Temp., ° F.	Pressure, P.S.I.A.	Water-Rich Liquid Mole Fraction of Propylene × 10^4	Propylene-Rich Liquid Mole Fraction of Water × 10^4
100.05	470.0	8.0886	9.012
100.00	1093.3	9.8059	8.331
100.00	1751.8	10.2631	7.699
100.20	2287.0	11.2611	7.328
100.05	2913.0	...	7.470
100.25	3188.0	12.2040	7.001
100.30	3513.5	12.9589	7.022
100.30	4122.7	13.1481	6.877
100.25	4781.0	13.4538	6.402
160.27	770.0	9.5567	36.135
160.20	929.0	9.6743	...
160.20	1277.0	...	35.630
160.30	1756.9	11.2017	...
160.30	2243.0	11.4832	...
160.15	2268.2	...	32.790
160.00	2748.4	...	30.180
160.30	3063.2	12.3313	30.890
160.20	3779.7	...	30.650
160.30	3893.0	13.9303	...
160.30	4058.5	...	30.110
160.30	4667.7	14.0519	...
160.23	4791.7	...	28.310

Table III. Experimental Data in the Three-Phase Region

Temp., ° F.	Pressure, P.S.I.A.	Water-Rich Liquid Mole Fraction of Propylene × 10^4	Propylene-Rich Liquid Mole Fraction of Water × 10^4	Propylene-Rich Vapor Mole Fraction of Water × 10^4
100.30	234.3	8.932	8.537	38.463
121.50	305.4	8.777	18.053	51.644
141.30	380.0	8.913	27.224	72.900
160.35	467.7	9.458	40.956	86.660
182.10	578.2	10.005	53.174	104.142
194.70	661.0	10.478	66.935	104.336
197.80	675.4	...	96.542	95.126

These data are also shown on Figures 1–4 and 7–9. The graphically smoothed data are presented in Table IV, V, and VI. In Figures 1, 2, and 3 the solubility of propylene in water is shown at various pressures and temperatures for the two-phase and three-phase regions. In Figure 4 the solubility of propylene in water is compared with the solubility of other hydrocarbons in water at 100° F. (*1–6*) showing the trend of type and molecular weight of the hydrocarbon.

Figures 5 and 6 show the solubility of water in the propylene rich phases exhibiting the three-phase envelope. The three-phase critical conditions are shown at Figure 7. The three-phase critical conditions are: Temperature, 197.9° F; pressure, 676 p.s.i.a.; composition, 0.0096 mole fraction water.

In Figure 8 the solubility of water in the hydrocarbon-rich liquid is shown and compared with the work of other

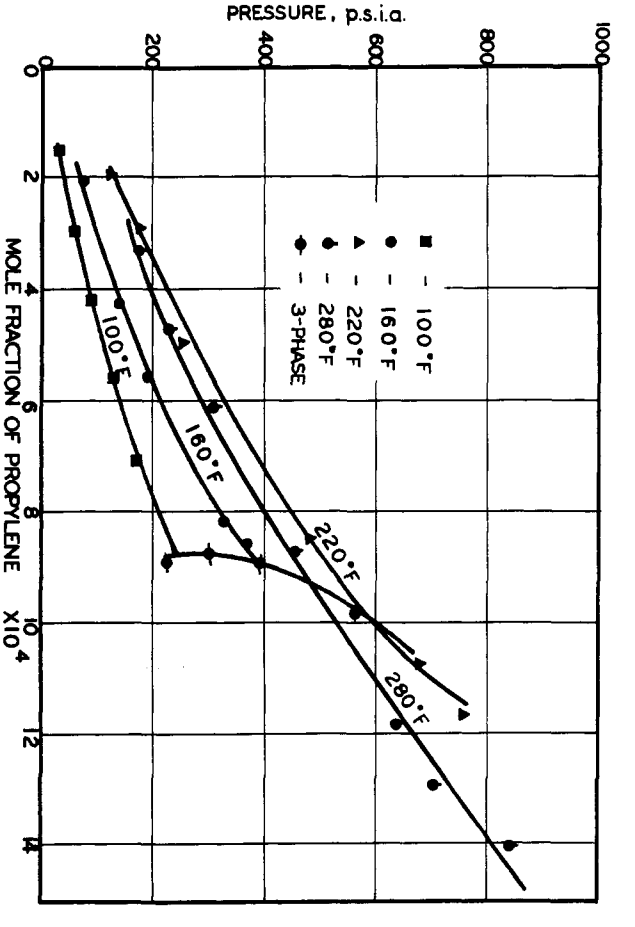

Figure 1. Solubility of propylene in water-rich liquid at low pressures

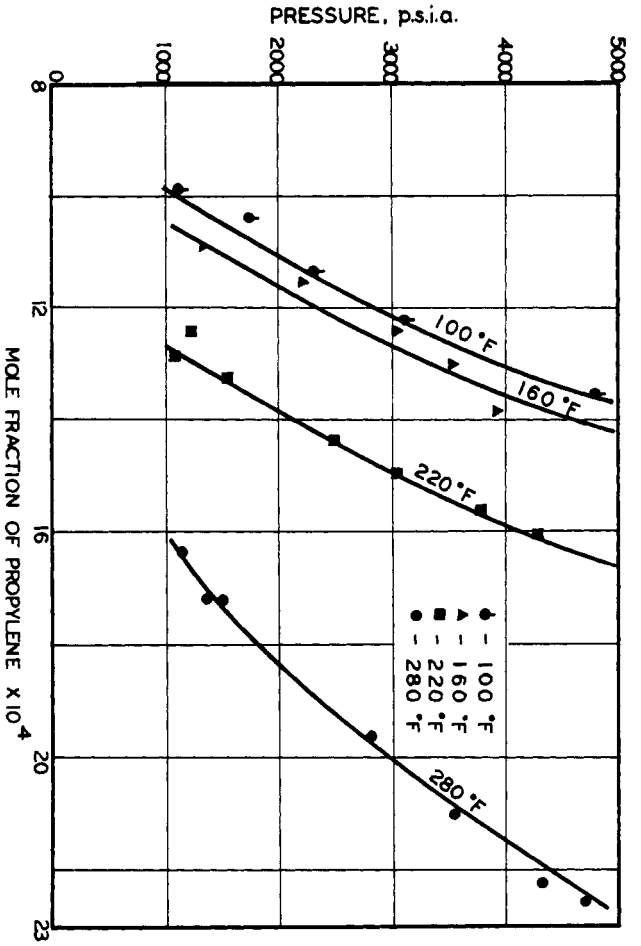

Figure 2. Solubility of propylene in water-rich liquid at high pressures

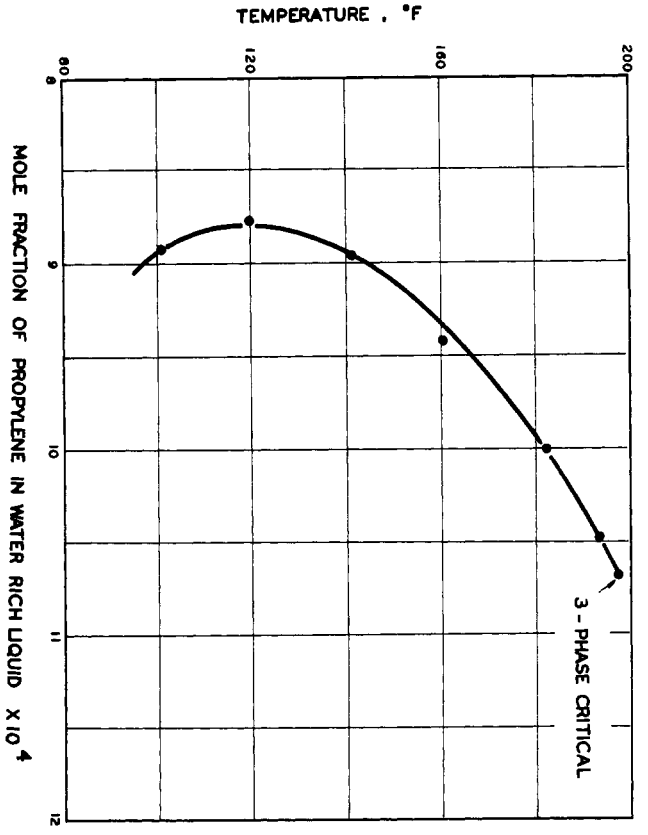

Figure 3. Solubility of propylene in 3-phase region

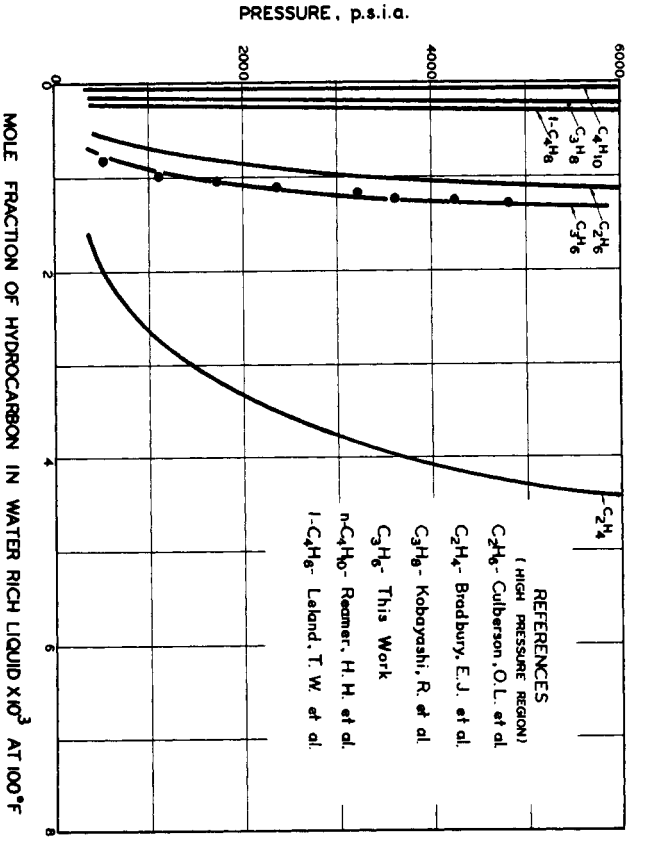

Figure 4. Solubility of hydrocarbons in water at 100° F.

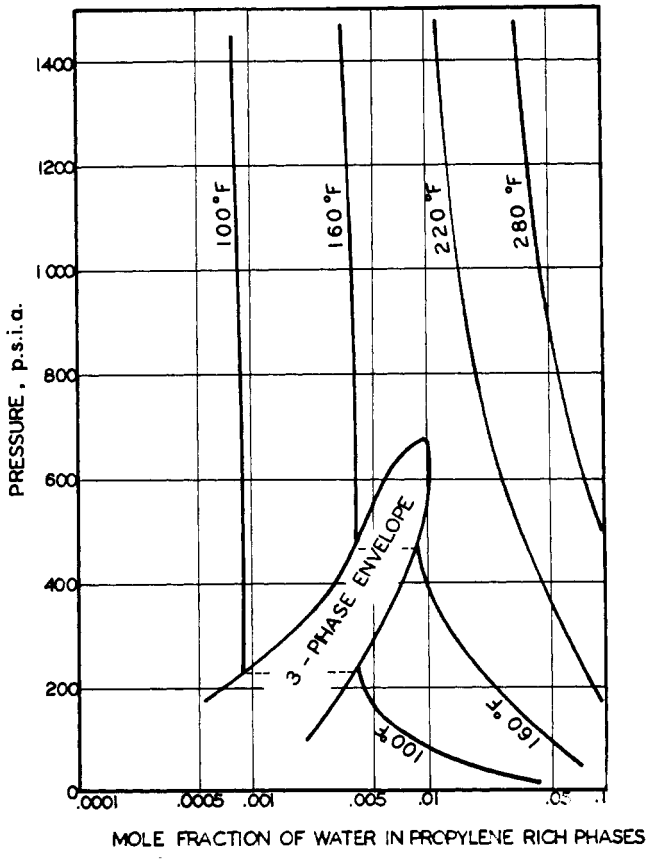

Figure 5. Solubility of water in propylene-rich phases at low pressures

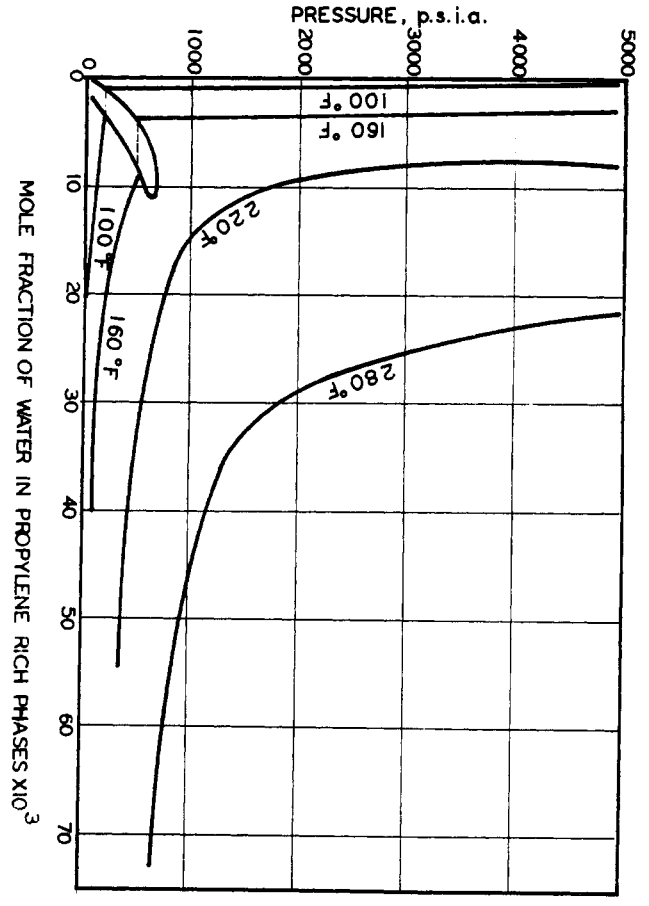

Figure 6. Solubility of water in propylene-rich phase at high pressures

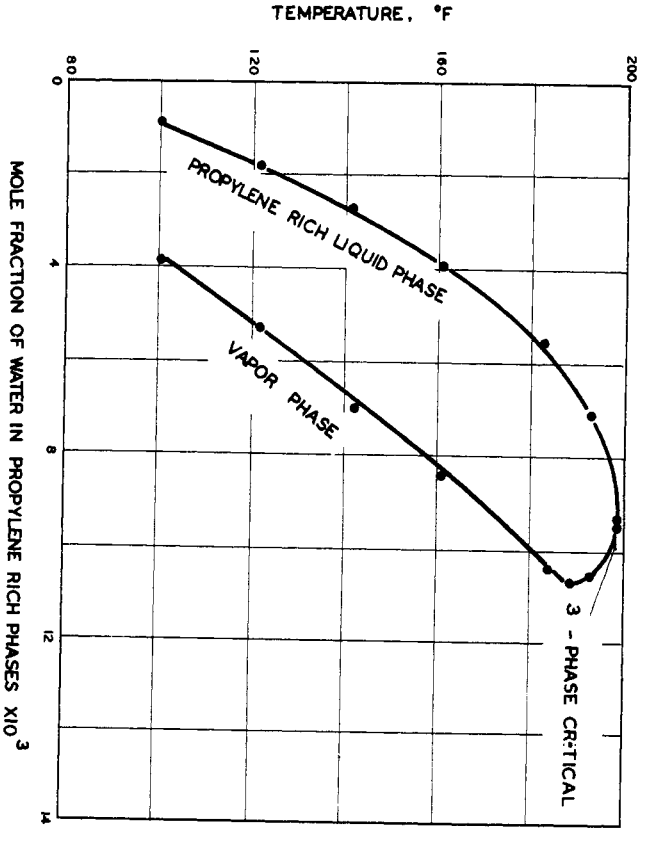

Figure 7. Solubility of water in 3-phase region

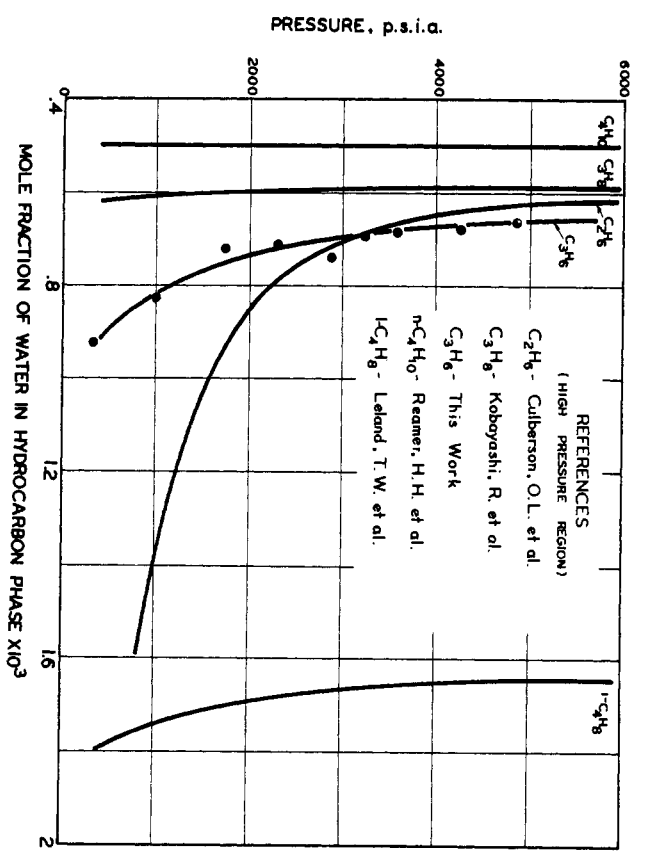

Figure 8. Solubility of water in hydrocarbons liquids at 100° F.

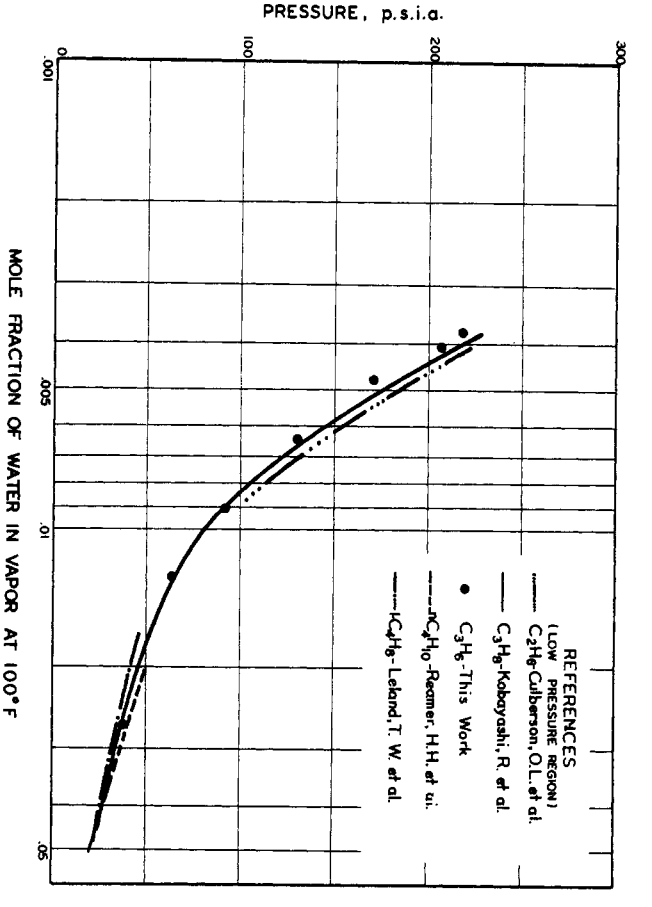

Figure 9. Solubility of water in hydrocarbon vapors at 100° F.

Table IV. Smoothed Data in the Two-Phase Vapor-Liquid Region

Temp., ° F.	Pressure, P.S.I.A.	Water-Rich Liquid Mole Fraction of Propylene × 10^4	Propylene-Rich Vapor Mole Fraction of Water × 10^4
100	50	2.175	166.0
100	75	3.420	112.0
100	100	4.505	85.8
100	125	5.405	66.0
100	150	6.195	52.3
100	175	6.915	44.0
100	200	7.603	40.0
100	225	8.250	38.0
160	75	2.080	633.0
160	100	3.040	478.5
160	150	4.480	310.5
160	200	5.600	215.5
160	250	6.570	175.0
160	300	7.460	142.0
160	350	8.296	120.0
160	400	8.990	100.0
160	425	9.243	98.3
220	150	2.430	1210.0
220	200	3.530	855.0
220	250	4.540	688.0
220	300	5.460	580.0
220	400	7.140	460.0
220	500	8.640	325.0
220	600	9.950	255.0
220	700	11.065	210.0
220	800	12.040	183.0
220	1000	12.170	150.0
220	1500	13.200	113.0
200	2000	13.870	93.4
220	2500	14.450	86.8
220	3000	14.950	82.7
220	3500	15.440	80.5
220	4000	15.740	79.3
220	4500	16.220	78.6
220	5000	16.620	78.1
280	300	6.090	1850.0
280	400	7.900	1242.0
280	500	9.600	950.0
280	600	11.240	794.0
280	700	12.780	690.0
280	800	13.980	606.0
280	900	14.750	528.0
280	1000	15.500	459.0
280	1250	16.625	377.0
280	1500	17.390	326.0
280	2000	18.470	284.0
280	2500	19.315	266.0
280	3000	20.100	251.0
280	3500	20.870	238.0
280	4000	21.630	225.0
280	4500	22.380	213.0

Table V. Smoothed Data in the Two-Phase Liquid-Liquid Region

Temp., ° F.	Pressure, P.S.I.A.	Water-Rich Liquid Mole Fraction of Propylene × 10^4	Propylene-Rich Liquid Mole Fraction of Water × 10^4
100	500	8.435	8.972
100	1000	9.420	8.422
100	1500	10.260	8.016
100	2000	10.940	7.690
100	2500	11.540	7.415
100	3000	12.120	7.183
100	3500	12.620	6.977
100	4000	13.000	6.775
100	4500	13.360	6.578
160	1000	9.940	36.020
160	1500	10.780	34.827
160	2000	11.440	33.667
160	2500	11.980	32.552
160	3000	12.500	31.560
160	3500	12.970	30.685
160	4000	13.400	29.912
160	4500	13.800	29.915
160	4750	...	28.890

Table VI. Smoothed Data in the Three-Phase Region

Temp., ° F.	Water-Rich Liquid Mole Fraction of Propylene × 10^4	Propylene-Rich Liquid Mole Fraction of Water × 10^4	Propylene-Rich Vapor Mole Fraction of Water × 10^4
100	8.927	10.08	37.90
110	8.782	13.00	45.70
120	8.765	17.80	53.50
130	8.817	22.70	61.43
140	8.920	27.90	69.32
150	9.075	33.25	77.05
160	9.290	38.70	84.82
170	9.575	44.90	92.68
180	9.925	52.66	100.75
190	10.315	64.80	108.10
191	10.350	66.50	108.20
195	10.500	75.10	105.90
197	10.615	81.80	101.50
198	10.650	93.50	93.50

investigators (2–6) on other hydrocarbons. Again the trend is shown for various molecular weights and types of hydrocarbons. In Figure 9 the water content of the hydrocarbon vapor is shown. Here the effect of the molecular weight and type of hydrocarbon is much less pronounced than for the liquid solubility.

Accuracy. A summary of the estimated accuracies of the measured variables and experimental errors are as follows:

Measured Variable	Estimated Accuracy	Max. Exptl. Error
Temperature	±0.1° F.	...
Pressure	±0.5 p.s.i.	Pressure fluctuates ±1.0 p.s.i. during sampling period

Concentration:

Water-rich liquid	4.1% based on smoothed curve
Hydrocarbon-rich liquid	4.8% based on smoothed curve
Hydrocarbon-rich vapor	2.7% based on smoothed curve

ACKNOWLEDGMENT

Phillips Petroleum Co. furnished the propylene.

LITERATURE CITED

(1) Bradbury, E.J., McNulty, D., Savage, R.L., McSweeney, E.E., *Ind. Eng. Chem.* **44**, 211–12 (1952).
(2) Culberson, O.L., McKetta, J.J., *Trans. A.I.M.E.* **192**, 297–300 (1951).
(3) Kobayashi, R., Katz, D.L., *Ind. Eng. Chem.* **45**, 440–6 (1953).
(4) Leland, T.W., McKetta, J.J., Kobe, K.A., *Ibid.*, **47**, 1265-71 (1955).
(5) Reamer, H.H., Olds, R.H., Sage, B.H., Lacey, W.N., *Ibid.*, **36**, 381–3 (1944).
(6) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ibid.*, **44**, 609-15 (1952).
(7) Wehe, A.H., Ph.D. dissertation, University of Texas, Austin, Tex., 1960.
(8) Wehe, A.H., McKetta, J.J., J. CHEM. ENG. DATA **6**, 167–72 (1961).
(9) Wehe, A.H., McKetta, J.J., *Anal. Chem.* **33**, 291–3 (1961).

RECEIVED for review October 19, 1962. Accepted February 18, 1963. Work supported by National Science Foundation.