

Solubility of Propylene in Water

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Although a considerable amount of work has been published on the high pressure solubility of the permanent gases, such as hydrogen and nitrogen as well as some of the light hydrocarbon gases, very little information has been published on the solubility of the unsaturated hydrocarbons over any wide pressure and temperature range.

Some of the investigations on the unsaturated hydrocarbons include those of Hiraoka (9), who studied the solubility of acetylene in water at pressures up to 500 p.s.i. and temperatures to 86° F., Bradbury, and others (2) on the solubility of ethylene in water at pressures up to 8000 p.s.i. and temperatures to 212° F., and Brooks and McKetta (3-5) who published information on the phase behavior of the 1-butene-water system including the three phase region, the vapor-liquid equilibrium, and the liquid-liquid equilibrium.

Data were obtained in this present investigation on the solubility of propylene in water at temperatures from 70° to 220° F. and pressures from atmospheric to 500 p.s.i.a.

EXPERIMENTAL METHODS

Apparatus. The apparatus was similar to that used by Brooks and McKetta (3) and Culberson, Horn, and McKetta (6). An equilibrium cell was charged with propylene and water, then rocked for several hours at a constant temperature and pressure. When rocking was stopped, the cell was placed in a vertical position, and the liquid phase was sampled directly into the analytical train, after one half hour was allowed for separation of the phases in the cell.

Analytical. This analytical technique is an absolute one rather than a relative one used by most investigators of this type of solubility work (2-7, 9). The method was described by Azarnoosh and McKetta (7). Approximately 400 ml. of the water-rich liquid phase are removed from the equilibrium cell into a distillation flask. The flask is heated, driving off the dissolved gases, and the resulting gases (saturated with water vapors) are collected and the volume of gases determined. Corrections were made for the water content of these effluent gases. The boiling is continued until the resulting pressure measurement indicates that the system is composed of pure water. Reproducible results, within $\pm 2\%$ were obtained on representative samples using this analytical method.

Materials Used. The water was boiled, distilled water. Research grade propylene was obtained from the Phillips Chemical Co. The purity was 99.91% and no additional purification was attempted.

DISCUSSION OF RESULTS

The experimentally determined solubility of the propylene in the water-rich phase is shown in Table I. During the entire investigation this system was in the two-phase region. At no time did the pressure exceed the vapor pressure of the propylene above which pressure the third phase begins to appear. The equilibrium in this study is that between the hydrocarbon-rich vapor and the water-rich liquid. Included in Table I are the experimental data at 70° F. of Haughn and McKetta (8).

The experimental data were plotted on large pressure-com-

Table I. Experimental Data in the Two-Phase Region
 (Concentration of propylene in water-rich liquid phase)

70° F. ^a		100° F.		160° F.		220° F.	
Total pressure, p.s.i.a.	Mole frac. propylene $\times 10^4$	Total pressure, p.s.i.a.	Mole frac. propylene $\times 10^4$	Total pressure, p.s.i.a.	Mole frac. propylene $\times 10^4$	Total pressure, p.s.i.a.	Mole frac. propylene $\times 10^4$
21.7	1.66	23.3	1.122	22.7	0.450	44.2	0.560
77.4	5.99	35.3	1.883	45.7	1.020	70.5	1.129
136.3	8.28	37.25	1.657	77.0	1.605	95.7	1.305
144.7	9.48	41.9	1.921	108.7	2.540	122.2	2.325
		49.5	2.426	109.7	2.539	143.7	2.655
		70.0	3.258	110.7	2.420	168.7	3.154
		79.4	3.544	111.2	2.475	196.7	3.741
		79.9	3.723	142.7	3.257	219.7	4.150
		100.0	4.184	150.7	3.440	236.7	4.860
		102.95	4.996	186.7	4.350	254.7	4.940
		117.2	5.000	216.7	5.070	275.7	5.584
		121.7	4.997	253.2	5.712	298.2	5.769
		138.7	5.734	296.2	6.500	300.2	5.750
		155.7	6.454	298.2	6.580	325.7	6.363
		157.2	6.320	298.2	6.527	353.2	6.853
		162.2	6.685	298.2	6.433	367.7	7.270
		174.2	7.199	328.7	7.182	389.7	7.600
		187.7	7.846	335.7	7.095	392.7	7.500
		198.7	8.409	366.2	7.560	414.7	7.872
		207.7	8.362	374.7	7.550	435.7	8.107
		209.2	8.600	465.7	8.490	455.7	8.515
		232.7	9.390	485.7	8.788	493.7	9.123
		240.7	9.506	490.7	8.710	496.7	8.900

^aFrom data of Haughn and McKetta (8).

position diagrams, such as the ones shown in Figure 1. The smoothed data taken from Figure 1 are shown in Table II. Additional smoothed data at 130° and 190° F. taken from cross plots are also shown in Table II. The smoothed data from Table II were plotted as a temperature-composition diagram as shown in Figure 2. In Figure 2 is shown also the approximate location of the three-phase locus, although this region was not studied during this investigation. Figure 2 shows that the minimum solubility phenomenon exists at pressures above 350 p.s.i.a. Most of the saturated light hydrocarbons have exhibited minimum solubility (1, 6, 7, 10).

A comparison of the solubility of the various light hydrocarbons is shown in Figure 3 at 100° F. These include the 100° F. data extrapolated from the work on acetylene by Hiraoka (9); data on ethylene, Bradbury and others (2); solubility data on methane, Culberson and McKetta (7); solubility data on ethane, Culberson, Horn, and McKetta (6); data on propane, Azarnoosh and McKetta (1); data on the butane-

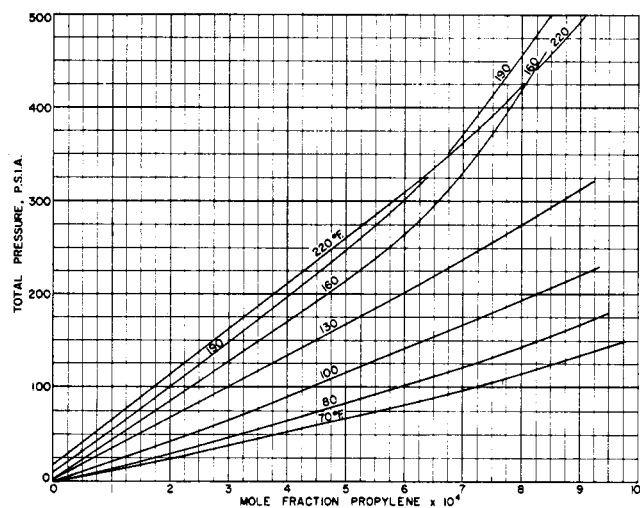


Figure 1. Effect of pressure on solubility of propylene in liquid water

Table II. Smoothed Data in Two-Phase Region
(Concentration of propylene in water-rich liquid phase in mole fraction $\times 10^4$)

Pressure, p.s.i.a.	Temperature, °F.					
	70°	100°	130°	160°	190°	220°
14.7	1.36	0.76	0.42	0.27	0.13	...
20	1.78	0.92	0.56	0.40	0.25	0.08
40	3.12	1.85	1.16	0.88	0.68	0.49
60	4.52	2.76	1.76	1.35	1.12	0.90
80	5.86	3.55	2.38	1.82	1.53	1.30
100	7.14	4.33	2.96	2.30	1.96	1.72
120	8.24	5.10	3.59	2.77	2.41	2.12
140	9.32	5.87	4.16	3.25	2.83	2.52
160	...	6.64	4.76	3.71	3.25	2.94
180	...	7.40	5.32	4.20	3.65	3.35
200	...	8.17	5.92	4.64	4.06	3.75
220	...	8.93	6.49	5.07	4.45	4.16
240	7.05	5.48	4.84	4.57
260	7.60	5.87	5.22	4.98
280	8.14	6.22	5.61	5.39
300	8.68	6.55	5.97	5.80
320	9.16	6.84	6.31	6.22
340	7.11	6.57	6.60
360	7.35	6.85	6.96
380	7.58	7.11	7.30
400	7.80	7.34	7.63
420	8.02	7.58	7.95
440	8.22	7.82	8.27
460	8.41	8.05	8.57
480	8.28	8.84
500	8.49	9.11

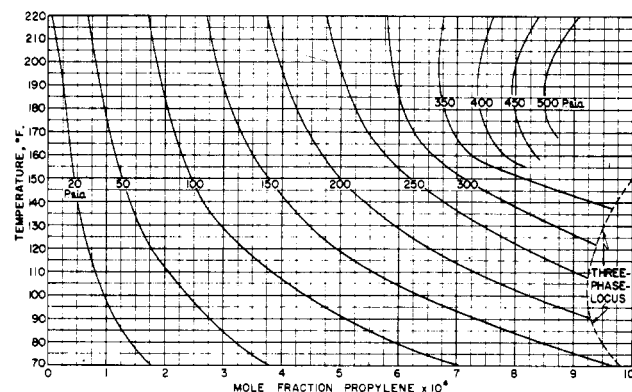


Figure 2. Temperature-composition diagram for the solubility of propylene in liquid water

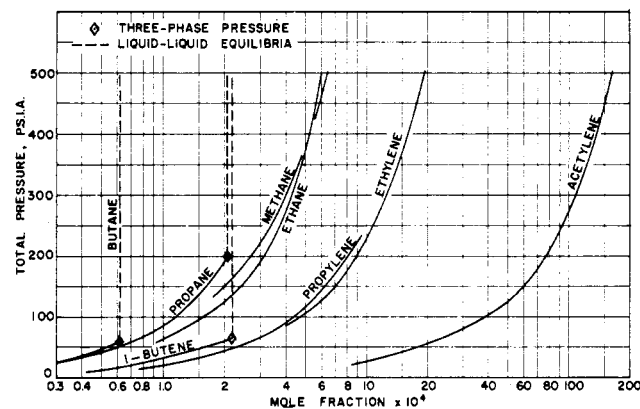


Figure 3. Comparison of solubility of various hydrocarbons in liquid water at 100° F.

water system, Reamer, Sage, and Lacey (10); and data on 1-butene-water system, Brooks and McKetta (3). The propylene data on Figure 3 are taken from Figure 1 and Table II. Almost throughout the range of pressures indicated in Figure 3, acetylene is approximately 10 times more soluble in water than ethylene, propylene, or 1-butene.

Figure 1 shows that propylene tends to follow Henry's Law over quite a wide pressure range. Because the vapor pressure of water is so low compared to that of the propylene, Figure 1 approximates a partial pressure-composition diagram.

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) Azarnoosh, A., McKetta, J. J., *Petrol. Refiner* **37**, No. 11, 275 (1958)
- (2) Bradbury, E. J., McNulty, D., Savage, R. L., McSweeney, E. E., *Ind. Eng. Chem.* **44**, 211 (1952).
- (3) Brooks, W. B., McKetta, J. J., *Petrol. Refiner* **34**, No. 2, 143 (1955).
- (4) *Ibid.*, No. 4, p. 138.
- (5) Brooks, W. B., Haughn, J. E., McKetta, J. J., *Ibid.*, **34**, No. 8, 129 (1955).
- (6) Culberson, O. L., Horn, A. B., McKetta, J. J., *Trans. Am. Inst. Mining Met. Engrs., Petrol. Div.* **189**, 1 (1950).
- (7) Culberson, O. L., McKetta, J. J., *Ibid.*, **192**, 223 (1951).
- (8) Haughn, W. F., McKetta, J. J., unpublished data.
- (9) Hiraoka, H., *Rev. Phys. Chem., Japan* **24**, No. 1, 13 (1954).
- (10) Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **44**, 609 (1952).

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