Solubility of Propyne in Water

RUBEN F. INGA[1] and JOHN J. McKETTA
University of Texas, Austin, Tex.

THE SOLUBILITY of propyne (methylacetylene) in water was studied at pressures to 200 p.s.i.a. for a temperature range of 70° to 220° F. No data have been found in the literature for the solubility of propyne in water.

EXPERIMENTAL METHODS

Equilibrium. Tha apparatus used to attain equilibrium included a rocking autoclave, described by Brooks and McKetta (*1*) and Culberson, Horn, and McKetta (*2*). The cell was charged with propyne and water, rocked for 1 hour at constant temperature, then kept at rest for 30 minutes to allow complete separation of the phases. The liquid phase was then sampled directly into the analytical train. The rocking and settling time were determined in the manner discussed by Culberson, Horn, and McKetta (*2*).

Analytical. The absolute method of analysis described by Davis and McKetta (*3, 4*) was used. The results by this method had an average deviation of ±2 × 10^{-5} mole fraction.

Table I. Experimental Data on Solubility of Propyne in Water

Temp., ° F.	Total Pressure, p.s.i.a.	Mole Fraction × 10^4	Temp., ° F.	Total Pressure, P.S.I.A.	Mole Fraction × 10^4
70	17.4	12.24	160	17.9	6.16
	20.9	20.74		28.4	9.49
	25.4	24.88		43.4	13.91
	29.4	26.82		53.4	17.83
	30.9	30.12		62.4	21.18
	39.9	36.41		63.4	21.84
	41.4	39.09		82.4	29.00
	48.4	43.52		100.8	33.78
	55.9	48.84		169.5	51.15
	60.9	54.01			
	63.9	55.89			
	71.4	63.95			
	76.4	66.83	220	20.9	1.40
				53.9	10.08
				74.4	15.06
100	23.9	15.42		94.9	20.05
	41.9	26.69		112.8	25.39
	46.9	32.25		132.3	28.51
	53.9	34.29		151.8	33.85
	59.9	39.84		170.8	37.72
	70.4	45.04			
	80.4	49.94			
	102.8	60.04			
	116.9	67.72			

Table II. Smoothed Data of Propyne Solubility in Two-Phase Region

	Temperature, ° F.					
	70	100	130	160	190	220
Pressure, P.S.I.A.	Concentration of Propyne in Water-Rich Liquid Phase, Mole Fraction × 10^4					
5	5.1	3.1	1.4	0.4	[a]	[a]
10	9.6	6.5	4.0	2.2	0.5	[a]
14.7	14.6	9.9	6.5	4.0	1.6	[a]
20	19.4	13.3	9.3	6.5	3.5	1.5
30	29.2	20.2	14.7	10.6	6.9	3.9
40	37.4	26.7	29.8	14.3	10.2	6.7
50	45.6	33.2	24.5	18.4	12.4	9.2
60	54.3	39.2	28.5	21.7	16.5	11.6
70	63.2	44.9	32.5	25.0	19.2	14.4
80	...	50.4	37.0	27.9	21.8	16.5
90	...	55.8	41.2	31.1	24.3	19.0
100	...	61.6	45.3	34.3	28.0	21.6
120	...	69.4	51.9	39.4	32.1	26.4
140	...	...	58.3	44.2	36.4	30.9
160	...	...	64.8	49.3	41.0	35.5
180	...	...	70.9	53.6	44.8	40.1
200	...	...	...	57.9	48.3	43.5

[a] Above boiling temperature of solution.

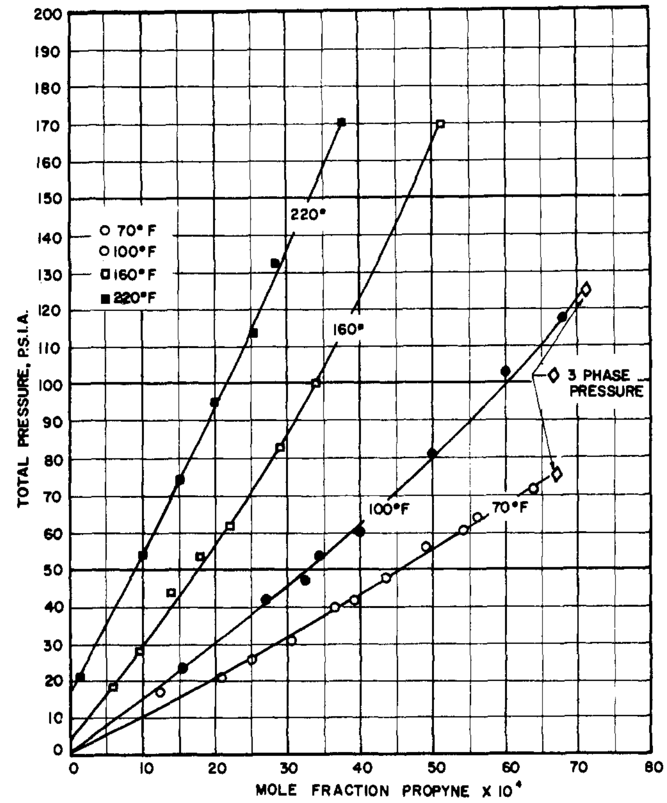

Figure 1. Solubility of propyne in water

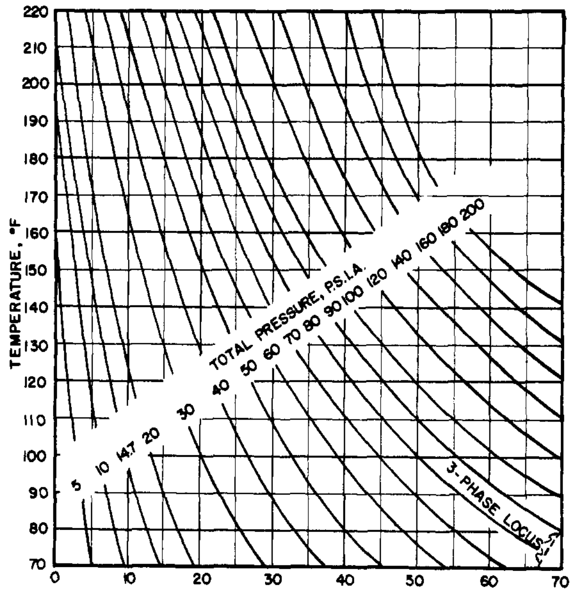

Figure 2. Temperature-composition diagram for water-rich phase

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[1] Present address, International Petroleum Co., Talaria, Peru.

Materials. Degassed, distilled water was used. The propyne was a technical grade (95%) supplied by the Air Reduction Co. and further purified by fractionation by the Phillips Petroleum Co. A mass spectrometer analysis of the purified propyne showed the purity to be 99.99 mole %.

DISCUSSION OF RESULTS

The experimental data are given in Table I and in Figure 1, where the solubility is shown as a function of the total pressure of the system. The smoothed data given in Table II were taken from the pressure-composition figures and plotted on a temperature-composition diagram in Figure 2. Figure 2 shows that propyne does not exhibit the minimum solubility phenomena in this pressure and temperature range.

ACKNOWLEDGMENT

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Solubilities of Various Hydrocarbons in Methanol

ROBERT W. KISER, G. DANA JOHNSON, and MARTIN D. SHETLAR
Department of Chemistry, Kansas State University, Manhattan, Kan.

IN STUDIES of complexes of urea and thiourea with various hydrocarbons (*14*) it was necessary to know the solubilities of these hydrocarbons in methanol. A literature search showed that data on the solubilities of hydrocarbon-methanol systems were lacking for all but a few hydrocarbons. Because reliable data concerning the solubility parameter of methanol could not be found, even estimation of the desired information was prevented. Therefore, solubilities and critical solution temperatures of a number of hydrocarbons in methanol have been determined.

As a result of these investigations, a value is given for the solubility parameter of methanol ($\delta = 12.4$) considered sufficiently reliable that the solubilities of hydrocarbons other than those studied here may be estimated. This value is in fair agreement with empirically predicted values, but in poor agreement with the values derived from heat of vaporization and vapor pressure data.

Data are also presented which indicate that the solubility parameter of 2,2,4-trimethylpentane is 7.45 rather than 6.82 and that of 2,2,5-trimethylhexane is 7.50 rather than 7.04. Other information derived from these solubility studies is reported and discussed.

EXPERIMENTAL

Reagents. The hydrocarbons and methanol (Table I) were carefully checked for purity, and were used as received, or purified as described below. A Cary Model 11 recording spectrophotometer was used to scan the spectrum from 300 mμ to 205 mμ for these materials, unless otherwise stated. Gas-liquid partition chromatographic analyses were obtained on a 14-foot tri-(*m*-tolyl) phosphate column in a Fisher-Gulf Model 160 partitioner. From the information obtained, and the refractive indices taken with an Abbe refractometer, conservative estimates of the impurity levels were made.

Ultraviolet analysis of *n*-pentane (technical grade) indicated the absence of unsaturated compounds. Gas chromatographic analysis and ultraviolet absorption revealed a minor trace of benzene as impurity, estimated to be less than 0.05 mole %. Ultraviolet analysis of *n*-hexane indicated that unsaturated compounds were absent. Gas chromatographic analysis showed no impurities; the maximum impurity was estimated to be 0.05 mole %. Ultraviolet analysis of *n*-heptane indicated approximately 0.8 mole % of impurity, probably unsaturated in nature. *n*-Octane (practical grade) was purified by passage through short columns of silica gel (Davison, No. 12) until the unsaturated compounds were removed. The resulting material, after purification, contained an estimated maximum impurity of 0.2 mole %.

n-Nonane contained small amounts of unsaturated impurities. The *n*-decane contained some unidentified unsaturated material, the maximum impurity was estimated to be about 0.5 mole %. 2,2-Dimethylbutane contained some unsaturated compounds, the maximum impurity being estimated from ultraviolet spectra to be 0.1 mole %. Ultraviolet analysis of 2,3-dimethylbutane indicated a trace of benzene and approximately 1.5 mole % of unsaturated impurities. Unsaturated compounds were present in 3-methylheptane to about 0.3 mole % as determined by

Table I. Refractive Indices of Hydrocarbons Used

Hydrocarbon	Source[a]	Refractive Index Exptl.	Refractive Index Literature
n-Pentane	EOC	1.3583	1.35748 (2)
n-Hexane	FC	1.3794	1.37486 (2)
n-Heptane	EOC	1.3879	1.38764 (2)
n-Octane	EOC	1.3975	1.39745 (2)
n-Nonane	MCB	1.40545	1.40549 (2)
n-Decane	MCB	1.4116	1.4120 (3, 4)
3-Methylpentane	MCB	1.3762	1.3764 (4)
2,2-Dimethylbutane	MCB	1.36885	1.36876 (2)
2,3-Dimethylbutane	MCB	1.37500	1.37495 (2)
3-Methylheptane	MCB	1.3984	1.39495 (2)
2,2,4-Trimethylpentane	EOC	1.39145	1.39145 (2)
2,2,5-Trimethylhexane	MCB	1.3997	1.3996 (2)
Cyclopentane	MCB	1.4046	1.40645 (2)
Methylcyclopentane	MCB	1.4100	1.4097 (2)
Cyclohexane	MCB	1.4259	1.42623 (2)
Methylcyclohexane	MCB	1.42315	1.42312 (2)

[a] EOC, Eastman Organic Chemicals; FC, Fisher certified; MCB, Matheson, Coleman, and Bell.