Phase Equilibrium in the Ethylene-Water System

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The mutual solubilities of ethylene and water for the binary in the two-phase region were studied. Data were taken at temperatures of 100° to 280° F. at 60° intervals for the pressure range of 500 to 5000 p.s.i.a. This study was conducted to extend the available knowledge on the behavior of hydrocarbon-water binary systems. This information is of value in petrochemical and refining industries for use in the design of process dehydration units.

BRADBURY *et al.* (*3*) have reported data on the solubility of ethylene in water for temperatures to 212° F. and pressures to 7700 p.s.i.a. Diepen and Scheffer (*7, 8*) report P and T data and water composition in the vapor phase for pressures to 882 and 1500 p.s.i.a. for temperatures to 77° F. In this study the composition of water in the supercritical fluid phase and solubilities of ethylene in water are reported at temperatures of 100°, 160°, 220°, and 280° F. and pressures to 5000 p.s.i.a.

The equipment used in this investigation has been described by Wehe (*16, 17*). A modified Meeco Model W water analyzer was used to determine the water content in the vapor phase. The sampling procedure has been described by Anthony (*1*). An absolute manometer and Orsat gas buret were used to determine the ethylene content of the water phase. This technique has been described by Wehe and McKetta (*18*). Chemical materials used were Phillips pure grade ethylene and deaerated distilled water.

The experimental technique used in determining the water content of the hydrocarbon vapor phase was tested by comparing data for the propylene-water, *n*-butane–water, and ethane-water throughout the anticipated temperature range with the data of Li (*13*), Wehe (*17*), and Reamer *et al.* (*14, 15*). These comparisons are shown in Table I. Agreement was believed to be within the accuracy of the literature values in all cases.

The sampling technique for the water phase was tested by comparing data for the ethane-water binary with the data of Culberson and McKetta (*5*) and the data for the ethylene-water binary with the data of Bradbury *et al.* (*3*). The agreement is considered good (Table II).

The effect of pressure on the water content of the vapor is shown in Figure 1. Graphically smoothed values for mutual solubilities of ethylene and water are tabulated in Table III. Figures 2 and 3 illustrate the effect of temperature and pressure on the solubility of ethylene in water for the binary. A minimum solubility exists for each isobar, and tends to occur at lower temperatures as the pressure is increased. This same effect was observed by Culberson and McKetta (*5, 6*) for ethane and methane solubilities in water.

The solubility of ethylene in water can be correlated with the following thermodynamic relation

$$\ln\left(\frac{f_H}{x_H}\right)_L = \frac{\bar{V}_H}{RT}P + \ln H' \qquad (1)$$

where $\ln H' = \ln H + \frac{\bar{V}_H P_s}{RT}$.

The assumptions implicit in Equation 1 are constant temperature, constant moles of water, and $\bar{V}_H$ independent of pressure and of the change in composition of ethylene in water with pressure. The value of $(f_H)_L$ at equilibrium is equal to $(f_H)_v$, which may be set equal to $(X_H)_v(f_H^\circ)_v$, provided the Lewis and Randal rule for ideal solutions applies to the vapor.

The fugacity of pure hydrocarbon vapor may be obtained from experimental data, from a generalized fugacity coefficient chart, or from an adequate equation of state. If, in addition, the values of Henry's law constant and of the partial molal volume of ethylene in the liquid are known, the solubility of ethylene in the liquid may be calculated from the above equation. This equation may also be used to extrapolate experimental solubility data at low pressures to theoretical solubilities at high pressures by treating the partial molal volume and the modified Henry's constant as empirical constants. The experimental data should form a straight line when plotted according to Equation 1.

Krichevsky and Kasarnovsky (*10, 11*) have derived and plotted Equation 1, to calculate solubilities of hydrogen and nitrogen in water, and Wiebe and Gaddy (*19*) calculated solubilities of carbon dioxide in water.

Table I. Comparison of Experimental and Literature Values of Vapor Phase Data

Experimental Data			Literature Values		
T, ° F.	Pressure, p.s.i.a.	Y_{H_2O}	T, ° F.	Pressure, p.s.i.a.	Y_{H_2O}
Propylene-Water (*13*)					
160.0	178.2	0.02506	160.25	187.67	0.02306
160.2	181.7	0.02456	150.25	187.67	0.02306
159.9	177.8	0.02433	160.25	187.67	0.02306
		0.02370	160.25	187.67	0.02306
n-Butane–Water Vapor in Three-Phase Region (*15, 17*)					
160	124.7	0.0373	160.0	125.4	0.0338
	124.2	0.0334	160.0	124.9	0.0351
	125.7	0.0340			
		0.0329			
		0.0334			
		0.0330			
	126.0	0.0329			
		0.0332			
Ethane-Water (*14*)					
100.0	372.1	0.00267	100.0		0.00279
160.1	434.2	0.01134	160.0		0.01187
220.2	1458.2	0.01322	220.0		0.01396
279.9	1566.2	0.0367	280.0		0.0370

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Table II. Comparison of Ethane-Water and Ethylene-Water Liquid Phase Data with Literature

Ethane-Water

Temp., ° F.	Pressure, p.s.i.a.	Mole Fraction Ethane × 10^3	
		X (exptl.)	*X* (*5*)
160.1	504.7	4.070	4.170
160.0	2940.7	0.837	0.838
160.2	4004.7	1.028	0.951
220.1	4085.7	1.153	1.163
220.1	3774.7	1.180	1.185

Ethylene-Water

Temp., ° F.	Pressure, p.s.i.a.	Mole Fraction Ethylene × 10^3	
		X (exptl.)	*X* (*3*)
100	3000	3.833	3.800
100	1000	2.265	2.350
160	1000	2.265	2.350
220	2000	3.350	3.350
220	1000	2.888	2.978

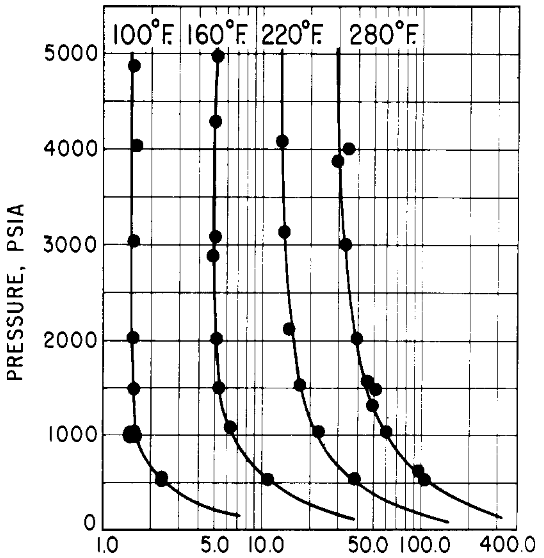

Figure 1. Water content of ethylene vapor for binary mixture

Table III. Smoothed Values for Mutual Solubilities of Ethylene and Water in Vapor-Liquid Region

Pressure, p.s.i.a.	*T* = 100° F.	*T* = 160° F.	*T* = 220° F.	*T* = 280° F.
	Mole Fraction Ethylene in Water × 10^3			
200	0.838	0.585	0.567	0.545
400	1.557	1.112	1.100	1.079
500	1.875	1.344	1.346	1.320
1000	2.955	2.355	2.281	2.455
1500	3.351	2.858	2.941	3.352
2000	3.574	3.159	3.351	3.970
2500	3.732	3.369	3.628	4.435
3000	3.830	3.545	3.872	4.836
3500	3.905	3.702	4.107	5.105
4000	3.954	3.840	4.333	5.535
4500	3.982	3.961	4.545	5.852
5000	3.999	4.085	4.751	6.180
	Mole Fraction Water in Ethylene × 10^3			
200	5.126	25.22	86.36	252.53
400	2.824	13.42	47.69	130.20
500	2.400	11.18	39.20	107.00
600	2.135	9.648	33.66	93.13
800	1.821	7.763	26.64	71.60
1000	1.661	6.675	22.60	60.03
1500	1.519	5.452	17.59	45.89
2000	1.535	5.037	15.47	38.62
2500	1.543	4.909	14.37	34.93
3000	1.550	4.910	13.83	32.59
3500	1.557	4.909	13.50	31.01
4000	1.559	4.900	13.32	29.94
4500	1.561	4.900	13.18	29.58
5000	1.563	4.900	13.10	29.08

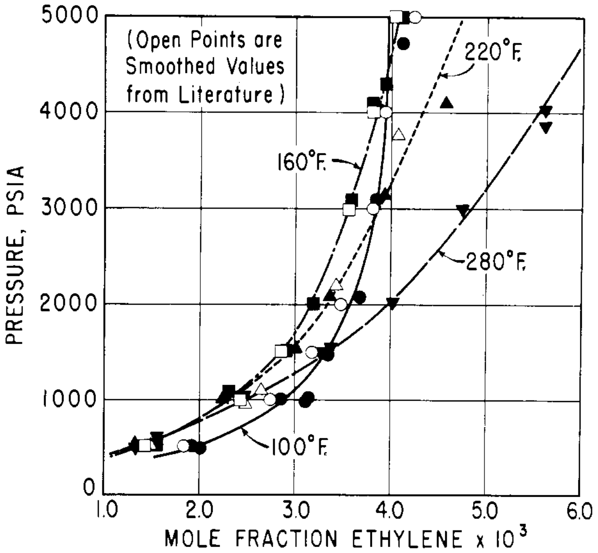

Figure 2. Effect of pressure on ethylene solubility for binary mixture

□ = 160° F.
○ = 100° F.
△ = 220° F.
▽ = 280° F.

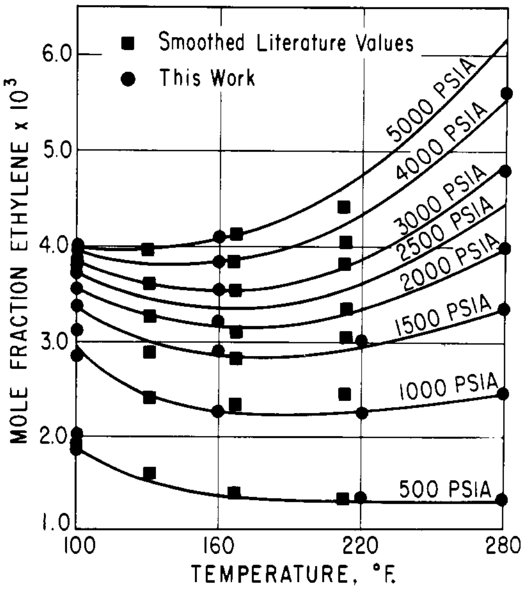

Figure 3. Effect of temperature on ethylene solubility for binary mixture

By use of experimental values of Henry's law constant and partial molal volumes of each gas in water, the solubility was calculated at pressures as high as 1000 atm. with excellent accuracy.

Kobayashi (*9*) plotted the solubilities of methane and other light hydrocarbons in water and Brooks (*4*) and Leland (*12*) plotted the solubility of 1-butene in water by use of Equation 1. Each of these investigators found that for the hydrocarbon systems, the experimental values showed considerable deviation from linearity as the pressures approached that of a phase change.

The solubility of ethylene in water was plotted according to Equation 1. This result is shown in Figure 4, and the values of $\bar{V}_H$ and ln H' are tabulated in Table IV. The values of the partial molal volumes and the modified Henry's constant were evaluated by two procedures. The first was to assume an ideal solution for the vapor. Therefore, $(f_H)_L = (f_H)_v = (X_H)_v(f_H{}^\circ)_v$. This method is the one used by Kobayashi (*9*), referred to here as the wet basis. The second procedure was to assume $(X_H) = 1.0$, and therefore $(f_H)_v = (f_H{}^\circ)_v$, referred to as the dry basis. The values of $\bar{V}_H$ and ln H' were determined by the least squares method of curve fitting with the use of the raw experimental data and the graphically smoothed data. The Benedict-Webb-Rubin equation of state was used to calculate fugacities of hydrocarbons (*2*).

The data were curve-fitted on the dry basis for engineering purposes. Very often when the solubility of a hydrocarbon in the liquid phase is desired an engineer does not know the water concentration in the vapor phase. Therefore, Equation 1 or Figure 4 would be more applicable for design calculations. The ethane solubilities reported by Culberson and McKetta (*5*) were also used to evaluate the values of $\bar{V}_H$ and ln H' for ethane over the pressure range of 500 to 5000 p.s.i.a. with both procedures by the method of least squares. These values are compared to those reported by Kobayashi (*9*) in Table IV. Kobayashi plotted the ethane-water data over the pressure range of 500 to 10,000 p.s.i.a. However, by use of the values calculated in this work on the dry or wet basis, the solubility of ethane in water at 10,000 p.s.i.a. was predicted to within 25% of Culberson's data for all temperatures as shown in Table IV.

Thermodynamically and graphically smoothed values of ethylene dissolved in water for the binary are tabulated in Table V. Experimental data for the ethylene water system are shown in Table VI.

Table IV. Modified Henry's Law Constants and Partial Molal Volumes of Dissolved Gases for Binaries

		100° F.	160° F.	220° F.	280° F.
		Ethane			
DB[a]	$\bar{V}$	0.8258	0.7573	0.7473	0.8543
	ln H'	13.2852	13.7819	13.8785	13.7511
WB	$\bar{V}$	0.8271	0.7608	0.7641	0.9966
	ln H'	13.2840	13.7778	13.8605	13.6637
Lit.	$\bar{V}$	0.849	0.858	0.917	1.021
(*9*)	ln H'	13.3113	13.7489	13.8088	13.6591
Comparison of predicted and experimental values at 10,000 p.s.i.a.					
DB	$X_{\text{calcd.}}$	0.00134	0.00146	0.00144	0.00254
	$X_{\text{exptl.}\ (5)}$	0.00113	0.00123	0.00150	0.00206
WB	$X_{\text{calcd.}}$	0.00134	0.00145	0.00194	0.00230
	$X_{\text{exptl.}\ (5)}$	0.00113	0.00122	0.00150	0.00206
		Ethylene			
Raw data					
DB	$\bar{V}$	0.8448	0.8275	0.7428	0.6361
	ln H'	12.1814	12.5588	12.7415	12.7550
WB	$\bar{V}$	0.8454	0.8310	0.7834	0.7855
	ln H'	12.1796	12.5513	12.7099	12.6504
Smoothed data					
DB	$\bar{V}$	0.7911	0.7567	0.8800	0.7435
	ln H'	12.2170	12.6208	12.6926	12.7088
WB	$\bar{V}$	0.7931	0.7654	0.9240	0.8894
	ln H'	12.2145	12.6111	12.6567	12.6084

$$\text{DB.}\quad \ln\left(\frac{f_v{}^\circ}{X}\right)_{HC} = \frac{\bar{V}}{RT}P + \ln H'$$

$$\text{WB.}\quad \ln\left(\frac{Yf_v{}^\circ}{X}\right)_{HC} = \frac{\bar{V}}{RT}P + \ln H'$$

[a] DB, dry basis.
WB, wet basis.

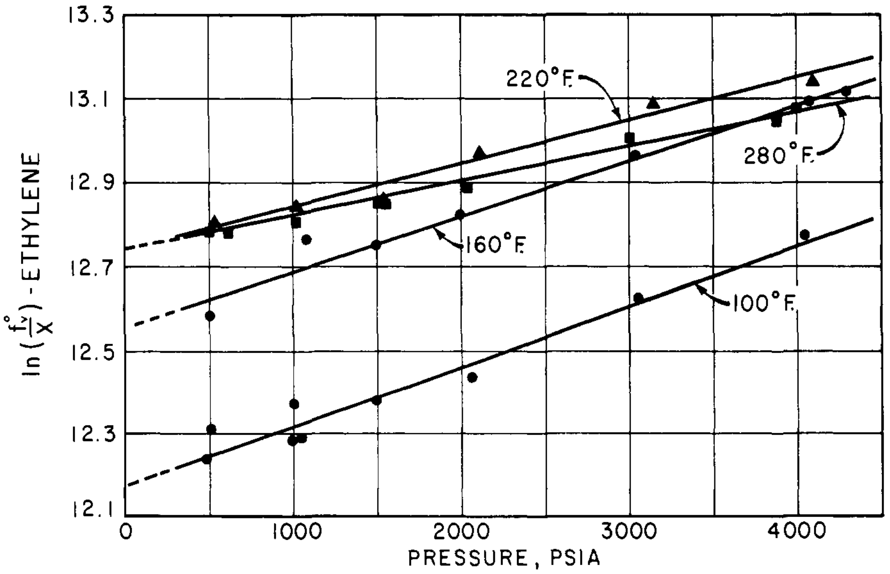

Figure 4. Equation 1 plotted for ethylene-water

Table V. Comparison of Thermodynamic and Graphically Smoothed Values for Ethylene-Water Binary

Pressure, p.s.i.a.	Mole Fraction of Ethylene in Water Phase × 10^3							
	100° F.		160° F.		200° F.		280° F.	
	X (GS)[a]	X (TS)	X (GS)	X (TS)	X (GS)	X (TS)	X (GS)	X (TS)
400	1.557	1.680	1.112	1.208	1.100	1.039	1.079	1.061
500	1.875	1.993	1.344	1.454	1.346	1.261	1.320	1.295
1000	2.955	3.012	2.355	2.389	2.281	2.173	2.455	2.300
2000	3.574	3.526	3.159	3.244	3.351	3.254	3.970	3.669
2500	3.732	3.657	3.367	3.455	3.628	3.575	4.435	4.136
3000	3.830	3.769	3.545	3.619	3.872	3.826	4.836	4.516
3500	3.905	3.867	3.702	3.759	4.107	4.034	5.195	4.836
4000	3.954	3.956	3.840	3.882	4.333	4.214	5.535	5.113
4500	3.982	4.038	3.961	3.993	4.545	4.374	5.852	5.360
5000	3.999	4.114	4.085	4.095	4.751	4.520	6.180	5.584

[a] GS, graphically smooth data.
TS, thermodynamically smooth data from Equation 1 on dry basis.

Table VI. Experimental Data on Ethylene-Water Binary

Temp., ° F.	Pressure, p.s.i.a.	Analysis, Mole Fraction	
		Water in HC vapor × 10^3	C_2H_4 in water phase × 10^3
160.0	517.7	10.955	1.555
160.1	1074.7	6.352	2.319
160.0	1501.2	5.374	2.921
159.9	2007.2	5.086	3.209
159.9	2887.2	4.971	4.134
99.9	497.2	2.363	2.012
99.9	1012.2	1.416	3.146
100.0	1483.2	1.495	3.388
100.1	2075.2	1.533	3.685
100.1	3067.2	1.579	3.720
100.1	4029.7	1.622	3.855
100.1	4724.2	1.545	4.125
160.1	4989.2	5.115	4.124
160.1	4289.7	5.110	3.945
160.0	4079.7	No vapor sample taken	3.826
160.0	3064.7	5.124	3.576
219.9	4099.7	13.24	4.589
220.2	3144.7	13.71	3.937
219.9	2102.2	14.86	3.368
219.9	1526.2	17.26	3.010
220.0	1018.2	22.79	2.240
220.1	534.2	37.37	1.329
279.7	616.7	95.98	1.540
279.8	1032.2	60.77	2.475
280.2	1499.2	51.89	3.264
280.1	2018.2	38.25	4.019
280.0	3002.2	32.93	4.728
279.9	4005.2	30.47	5.602
279.8	3874.7	29.83	5.631
280.0	1339.2	48.66	No liquid sample taken
279.9	1556.2	44.43	3.375
279.8	529.7	10.18	1.329
100.1	513.2	2.347	1.907
100.1	1002.2	1.542	2.854
99.9	1000.2	1.485	2.854
100.1	1000.2	1.532	3.134

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NOMENCLATURE

f = fugacity
f_i° = fugacity of pure component i at temperature and pressure of system
$\bar{V}_i$ = partial molal volume of component i in water phase
P = pressure
H = Henry's constant
H' = modified Henry's constant as defined by Equation 1
T = temperature
X = mole fraction of hydrocarbon in water
$(X_i)_v$, Y = mole fractions in vapor phase

Subscripts

v = vapor
i = component i
H = hydrocarbon
L = water-rich liquid phase
s = vapor pressure of solvent (water) at temperature of system

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