CRITICAL PRESSURES

Similarly, critical pressures reported by the investigators of each binary system (*5, 6, 7*) were plotted along the coordinates of a triangular plot in which the established critical compositions for the ternary system were included (Figure 2). Critical pressures at convenient intervals were determined as before (*1*) and were also included in the triangular plot.

When the compositions having the same critical pressure in the triangular plot were connected, curves were obtained which possessed a point of maximum propane composition for each critical pressure (Figure 2). Since the binary compositions having the same critical pressure could not be joined with a straight line, the results of this study indicate that, unlike the critical temperature, at least one experimental ternary point located near the center of the triangular plot is necessary to determine the complete critical pressure diagram for a ternary system.

LITERATURE CITED

(1) Cota, H.M., Thodos, George, J. Chem. Eng. Data **7**, 62 (1962).
(2) Etter, D.O., Kay, W.B., *Ibid.*, **6**, 409 (1961).
(3) Dourson, R.H., Sage, B.H., Lacey, W.N., *Trans. Am. Inst. Mining Met. Engrs.* **151**, 206 (1943).
(4) Grieves, R.B., Thodos, George, *Ind. Eng. Chem. Fundamentals* **1**, 45 (1962).
(5) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **42**, 534 (1950).
(6) Sage, B.H., Lacey, W.N., *Ibid.*, **32**, 992 (1940).
(7) Sage, B.H., Reamer, H.H., Olds, R.H., Lacey, W.N., *Ibid.*, **34**, 1108 (1942).

Received for review April 19, 1962. Accepted July 18, 1962.

Solubility of Methyl, Ethyl, and Vinyl Acetylene in Several Solvents

L. B. SIMPSON and F. P. LOVELL
Research Department, Imperial Oil Ltd., Sarnia, Ont., Canada

During a study of the removal of acetylene impurities from various hydrocarbon streams, it was necessary to determine the solubilities of three acetylene compounds in several solvents, such as water, methanol, and aqueous solutions of ammonium hydroxide, sodium hydroxide, and sodium chloride. The acetylene compounds were the methyl, ethyl, and vinyl homologs of the series. Each solubility, expressed as the Bunsen coefficient, was measured as a function of temperature in the range 0 to 60° C. for partial pressures of the order of 1 atm. These coefficients were also correlated with temperature. It was necessary to measure the solubilities of the acetylenes in the above solvents, since a literature search revealed no such information.

EXPERIMENTAL

Apparatus. The apparatus (Figure 1) consisted mainly of a glass manifold CFHK attached by vents to either a vacuum pump or the atmosphere; a gas buret and a mercury-filled manometer, both equipped with mercury leveling bulbs; a source of gas supply and a vessel *I*, for holding the solvent in a thermostat. The apparatus consists entirely of glass connections except for a flexible connector between the manifold and the sample holder. This connector consisted of two pieces of glass tubing joined by three very short pieces of rubber vacuum tubing. Although the bulk of the surface was glass, there still was sufficient flexibility for shaking. The above hydrocarbons are readily soluble in rubber, and for this reason a minimum of rubber tubing was used. Since the results obtained for both increasing and decreasing temperature show no hysteresis effect, it was concluded that the apparatus gave reproducibly accurate results.

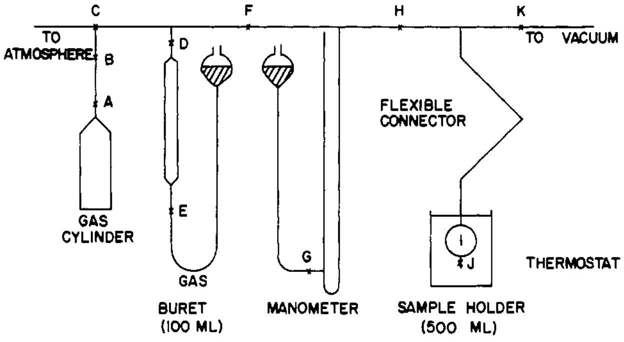

Figure 1. Apparatus for measureing acetylene solubilities

Procedure. Before each run, the whole system was flushed at least twice with nitrogen. The sample holder was disconnected from the manifold, filled with a known volume of solvent, reattached, and placed in the thermostat. These operations were carried out under an atmosphere of nitrogen. The temperature of the thermostat was set at 0° C., and the system was pumped out for approximately 15 minutes by attaching a vacuum pump at *K*. After this period, *K* was closed, and the system under vacuum was allowed to equilibrate. When equilibrium was reached, the pressure was read from the manometer. The difference between this and atmospheric pressure gives the vapor pressure of the solvent at 0° C. By changing the temperature of the thermostat, the vapor pressures were then measured at 30°, 45°, and 60° C. A knowledge of the vapor pressures at these temperatures, made it possible to check the apparatus—by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperatures. Such a plot should be linear, should extrapolate through the normal boiling point of the solvent in question, and should provide a value for the heat of vaporization of this solvent. In each of these experiments, all three criteria have been fulfilled.

When the operation of the apparatus had been checked, the actual determination of the solubility was made. The reaction flask was returned to 0° C. Valve *F* was closed and a volume of gas was introduced into the gas buret. The pressure of the gas in the buret was reduced to atmospheric by means of the three-way valve *C*. When this was done, *C* was closed, *F* opened, and the volume of gas completely pressured into the apparatus. This process was then repeated until the partial pressure of the gas in the apparatus was approximately 30 cm. of mercury. Since the gas buret, as well as all the other parts of the apparatus, had previously been calibrated, it was a simple matter to calculate the quantity of gas which had been introduced into the system.

When the partial pressure of gas reached approximately 30 cm. of mercury, gas addition was stopped, and the reaction vessel was shaken vigorously in the thermostat until equilibrium was attained, as noted by the reading on the manometer. The final pressure was then read. Knowing the volume of vapor space and the solvent vapor pressure, it was easy to calculate the moles of gas in the vapor space and hence the dissolved gas by difference.

This process was repeated at the other temperatures. As a check against hysteresis, the solubilities were determined for 0°, 30°, 45°, and 60° C. and the repeated for 45°, 30°, and 0° C. in that order. In this way, any leaks in the apparatus or other loss of gas could easily be detected.

Chemicals. The vinyl acetylene (E.I. du Pont de Nemours and Co.) was analyzed by vapor liquid partition chromatography to be 99.9% pure. The methyl and ethyl acetylene, obtained from the Matheson Co., were similarly analyzed and found to be 95.7% and 95.6% pure compounds, respectively. In all the experiments involving either methyl or ethyl acetylene, corrections were made in the calculation to eliminate the effect of the impurities.

For ethyl acetylene, the impurity was shown by gas chromatographic analysis to be heavier than the ethyl acetylene and not absorbed by the solvents. The effect of this impurity could therefore be easily eliminated. For methyl acetylene, the remaining impurity was shown by gas chromatographic analysis to be lighter than methyl acetylene. In making the corrections for this impurity, the Bunsen coefficient of the impurity was assumed to be of the same order of magnitude as that of the methyl acetylene.

All the other materials used in these experiments were reagent grade chemicals, and the water was distilled and degassed.

Errors and Accuracy. There are two main sources of error in these results: The ideal gas laws corrected only for the impurities in the methyl and ethyl acetylene have been used in all of these calculations. Only the solvent holder is thermostatted, the rest of the apparatus being kept at room temperature. This introduces some error into the results but since the volume of the thermostatted solvent holder is large relative to the volume of the rest of the system, and since room temperature is not too much different than operating temperature, it is felt that such an error will not be significant.

Because of the large solubility of these materials in methanol, a large number of gas additions and a small volume of solvent were required. For this reason, the standard deviation of the results involving methanol is ±10% whereas the standard deviation of all the others is ±5%.

Table I. Solubility of Methyl, Ethyl, and Vinyl Acetylene in Water, Methanol, and 3 Wt. % Ammonium Hydroxide

Temp., ° C.	Density of Solvents	Methyl Acetylene		Ethyl Acetylene		Vinyl Acetylene	
		Acetylene pressure, atm.	Bunsen[a] coeff., α	Acetylene pressure, atm.	Bunsen coeff., α	Acetylene pressure, atm.	Bunsen coeff., α
Solvent-Water							
0	0.9999	0.354	3.64	0.292	2.87	0.363	1.47
		0.336	3.90			0.359	1.50
30	0.9957	0.692	1.42	0.443	1.70	0.557	0.76
		0.660	1.53	0.505	1.39	0.549	0.78
45	0.9903	0.838	1.03			0.647	0.59
		0.836	1.04			0.643	0.60
60	0.9857	0.992	0.76	0.726	0.80	0.733	0.47
a[a]			1090		833		767
b[b]			−3.43		−2.60		−2.64
Solvent-Methanol							
0	0.8100	0.418	70.3	0.142	53.6	0.238	202
				0.335	84.2	0.194	229
30	0.7818	0.900	28.4	0.706	38.1	0.616	73
		0.636	32.4	0.590	43.3	0.519	80
45	0.7675	1.184	19.9			0.889	48
		0.836	23.0			0.769	52
60	0.7530	1.121	15.3	1.170	20.2	1.130	33
a			1010		970		1190
b			−1.86		−1.61		−2.06
Solvent-3 Wt. % Ammonium Hydroxide							
0	0.9880	0.356	3.97	0.363	2.84	0.395	1.96
		0.349	4.07				
30	0.9824	0.784	1.45	0.750	1.09	0.636	1.00
		0.768	1.49	0.736	1.12	0.627	1.02
45	0.9782	0.998	1.02			0.757	0.76
		0.990	1.03			0.749	0.77
60	0.9739	1.226	0.73	1.045	0.63	0.843	0.64
a			1140		1070		733
b			−3.57		−3.46		−2.41

[a] Bunsen coefficient $\alpha = Vo/VP$ where Vo is the volume of gas (STP) dissolved in V, the volume of liquid under a partial pressure of P atmospheres.

[b] Constants of the equation $\log_{10} \alpha = a/T + b$ where T is the absolute temperature, ° K.

Table II. Solubility of Ethyl Acetylene in Various Aqueous Solutions

Solvent, Wt. %			Temperature, ° C.					
			0	30	45	60	a^a	b^a
NH_4OH	0.3	Acetylene pressure, atm.	0.313	0.635 0.572		0.896		
		Bunsen coefficient, α^b	2.67	1.00 1.18		0.56	1110	−3.63
		Density of solvent	0.9987	0.9946	0.9899	0.9858		
	3.0	Acetylene pressure, atm.	0.363	0.750 0.736		1.045		
		Bunsen coefficient, α	2.84	1.09 1.12		0.63	1070	−3.46
		Density of solvent	0.9880	0.9824	0.9782	0.9739		
	10.0	Acetylene pressure, atm.	0.339	0.662 0.640		0.900		
		Bunsen coefficient, α	3.20	1.33 1.40		0.84	1010	−3.19
		Density of solvent	0.9627	0.9544	0.9500	0.9455		
NaOH	3.0	Acetylene pressure, atm.	0.358	0.645 0.648		0.997		
		Bunsen coefficient, α	1.48	0.52 0.54		0.16	1480	−5.22
		Density of solvent	1.0364	1.0285	1.0223	1.0150		
NaCl	20	Acetylene pressure, atm.	0.395 0.427	0.476 0.560	0.521	0.554		
		Bunsen coefficient, α	0.57 0.56	0.35 0.30	0.30	0.25	560	−2.29
		Density of solvent	1.1566	1.1429	1.1351	1.1268		
	25	Acetylene pressure, atm.	0.456	0.584 0.553	0.624 0.605	0.646		
		Bunsen coefficient, α	0.39	0.21 0.26	0.18 0.21	0.18	508	−2.27
		Density of solvent	1.1987	1.1834	1.1752	1.1666		

[a] Constants of the equation $\log_{10} \alpha = a/T + b$ where T is the absolute temperature, ° K.

[b] Bunsen coefficient $\alpha = V_0/VP$ where V_0 is the volume of gas (STP) dissolved in V, the volume of liquid under a partial pressure of P atmospheres.

Table III. Summary of Solubility Data

Solvent, Wt. %	Methyl Acetylene		Ethyl Acetylene		Vinyl Acetylene	
	a^a	b^a	a	b	a	b
Water	1090	−3.43	833	−2.60	767	−2.64
Methanol	1010	−1.86	970	−1.61	1190	−2.06
NH_4OH,						
0.3			1110	−3.63		
3.0	1140	−3.57	1070	−3.46	733	−2.41
10.0			1010	−3.19		
NaOH, 3.0			1480	−5.22		
NaCl,						
20			560	−2.29		
25			508	−2.27		

[a] Constants of the equation $\log_{10} \alpha = a/T + b$ where α is the Bunsen coefficient and T is the absolute temperature, ° K.

RESULTS AND DISCUSSION

The results obtained in these experiments are listed in Tables I to III. The Bunsen coefficient, defined as the volume of gas (STP), dissolved in volume, V, of liquid under a partial pressure of P atmospheres, is listed as a function of the temperature in Table I and II. For each experiment, the equilibrium partial pressure of the gas is also listed together with the density of the solvent as obtained from the International Critical Tables. The latter are included for ease of conversion to other units.

According to theory, the plot of the logarithm of the Bunsen coefficient *vs.* the reciprocal of the absolute temperature should be a straight line. Although no such plots are included, the results of all the experiments fulfilled this criterion very well. The constants, "a" and "b" which define the resulting straight lines and thereby represent the smoothed data are also given in Tables I and II and summarized in Table III for the experiments. From these values, the heat of solution of all of these materials is approximately 5 kcal. per mole.

In the aqueous solution, methyl and ethyl acetylene have almost equal solubilities and are both almost twice as soluble as the vinyl acetylene. On the other hand, in methanol, the methyl and ethyl acetylene still seem to have approximately equal solubilities but the vinyl seems to be the most soluble. The addition of ammonium hydroxide to the water hardly affects the solubilities of these compounds, but the addition of sodium chloride or sodium hydroxide produced a very marked salting out effect as might be expected.

RECEIVED for review January 29, 1962. Accepted May 31, 1962.