The root-mean-square deviation of the fit was 0.986 (sum of squares SS = 23.31) which is not as good as reported previously for many nonideal systems (*11*) probably because about half of the value of sum of squares is contributed by the first three experimental points (low 2-propanol concentration region). The calculated values of the boiling points appear in Table II.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical determinations.

Glossary

A_i, B_i, C_i	constants
B_{ii}, B_{ij}	second virial coefficient for pure component and the mixed virial coefficient, respectively
ΔH	heat of mixing
P, P_i°	total pressure, vapor pressure of pure component
R	gas constant
SS	sum of squares, $\sum_{i=1}^{N}(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})2_i$
t, T, T_i°	temperature: °C, K, and boiling temperature of pure component i
V_i°	molar volume of pure component
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficient

Literature Cited

(1) Boublikova, L., Lu, B. C. Y., *J. Appl. Chem.*, **19**, 89 (1969).
(2) Hwa, S. C. P., Ziegler, W. T., *J. Phys. Chem.*, **70**, 2572 (1966).
(3) Pimentel, G. C., McClellan, A. L., "The Hydrogen Bond", W. H. Freeman Co., San Francisco, 1960.
(4) Redlich, O, Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
(5) TRC Tables, "Selected Values of Properties of Chemical Compounds", and API 44, "Selected Values of Hydrocarbon and Related Compounds", Thermodynamics Research Center Data Project, College Station, Texas, 1961.
(6) Tsonopoulos, C., *AIChE J.*, **20**, 263 (1974).
(7) Tsonopoulos, C., *AIChE J.*, **21**, 827 (1975).
(8) Van Ness, H. C., "Classical Thermodynamics of Non-Electrolyte Solutions", Pergamon Press, London, 1964, pp 122, 125.
(9) Van Ness, H. C., Soczek, C. A., Peloquin, G. L., Machado, R. L., *J. Chem. Eng. Data*, **12**, 217 (1967).
(10) Wisniak, J., Tamir, A., *J. Chem. Eng. Data*, **20**, 168 (1975).
(11) Wisniak, J., Tamir, A., *Chem. Eng. Sci.*, **31**, 631 (1976).

Received for review January 15, 1979. Accepted December 10, 1979.

Solubility of Acetylene in Aqueous Solutions of Formaldehyde and 2-Butyne-1,4-diol[†]

Pandit B. Jadkar and Raghunath V. Chaudhari*

National Chemical Laboratory, Poona 411008, India

Solubility of acetylene in aqueous formaldehyde and 2-butyne-1,4-diol solutions was studied in a temperature range of 7–55 °C. The solubility of acetylene was found to be concentration dependent beyond 6.57 M of formaldehyde and 3 M of 2-butyne-1,4-diol. These data were correlated by using the following type of empirical equation: $\ln S = a + b/T + c \ln X$, which was found to fit the data satisfactorily. Heat of solution [$-\Delta H$] was also obtained from these data for the two systems studied.

Introduction

Solubility of gases in liquids is an important parameter in the interpretation of gas–liquid and gas–liquid–solid reactions. In models of such systems, solubility of the reactant gas in pure solvents does not always represent the solubility in solution, and the influence of other reactants and product must be accounted for in such cases. This work presents solubility data for acetylene in aqueous formaldehyde and 2-butyne-1,4-diol solutions. These data are likely to be useful in the design of reactors for 2-butyne-1,4-diol, which is manufactured from acetylene and aqueous formaldehyde in the presence of a solid catalyst (*1*, *2*). It is necessary to check the influence of formaldehyde and 2-butyne-1,4-diol on the solubility of acetylene in water, since such data are not available in the literature. In the present work, the effect of concentration of formaldehyde and 2-butyne-1,4-diol and temperature on solubility of acetylene in water was investigated.

[†] NCL Communication No. 2423.

Experimental Section

For gases having appreciable solubilities, the volumetric method could be conveniently used. An apparatus used in this work is schematically shown in Figure 1. A magnetically stirred vessel [A] provided with an outer jacket for circulating water at constant temperature (±0.05 °C) was used for saturation. In order to measure the volume of gas absorbed, we used a gas buret [B] of 100-cm^3 capacity, while a constant temperature during each experiment was maintained by using a thermostatic bath.

For preparation of solutions, degassed distilled water was used. Formaldehyde solution (38% w/v), supplied by M/s. HOC Ltd., and 2-butyne-1,4-diol of Fluka grade (Swiss make, 99.8% purity) were used directly for preparing samples of desired concentrations. Acetylene gas was passed through silica gel traps, to remove traces of acetone. The purity of acetylene, as analyzed by GC, was about 99.2%. Formaldehyde content was estimated by a volumetric method (*3*), while 2-butyne-1,4-diol was determined by a UV spectrophotometer. The values of the molar absorptivity ϵ and the wavelength for maximum absorbence, λ_{max}, used for analysis of 2-butyne-1,4-diol were 3.561×10^2 L mol^{-1} cm^{-1} and 286 mμ, respectively.

In a typical experiment, the system was first evacuated by using a high vacuum system and then acetylene gas was filled by careful control of stopcock [C1] and a two-stage-bubbler [G] shown in Figure 1. This evacuation–filling cycle was repeated three to four times to ensure complete flushing. Then acetylene saturated water from reservoir [S] was introduced into the buret [B] and the initial zero level reading was adjusted. After this, a known volume of formaldehyde or 2-butyne-1,4-diol solution was introduced into the saturation vessel [A] and the

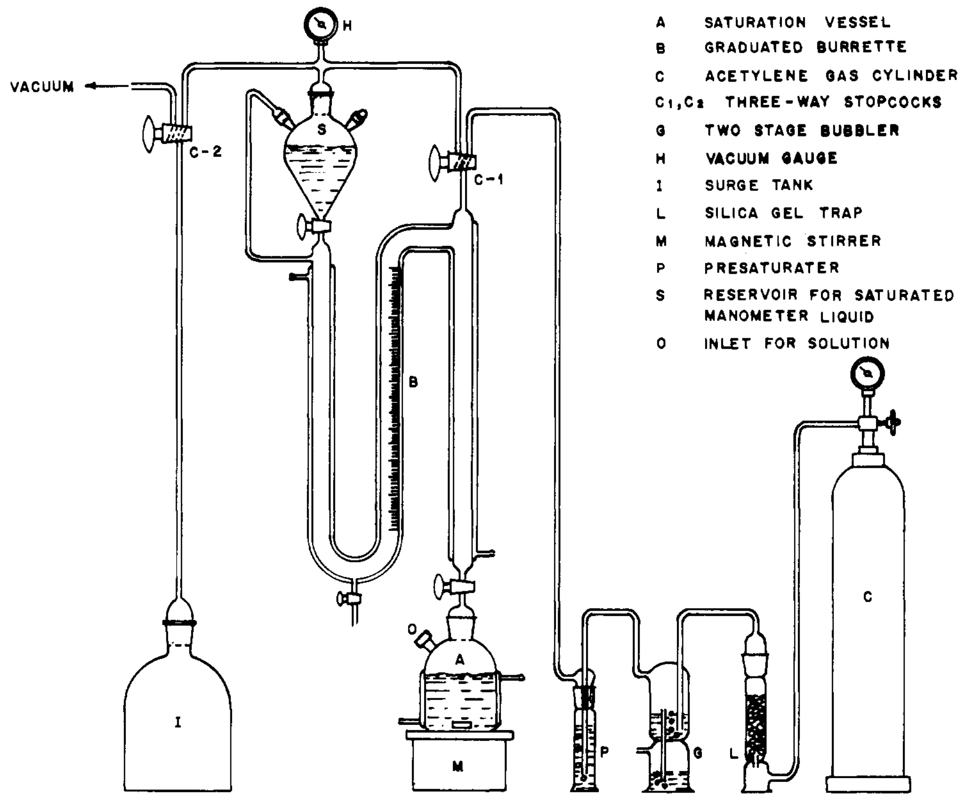

Figure 1. Schematic diagram of the experimental setup.

Table I. Solubility Data for the Acetylene-Formaldehyde-Water System

concn of formaldehyde, 10^3X, g-mol cm^{-3}	temp, K	solubility, 10^5S, g-mol cm^{-3} atm^{-1}
0	280	6.98
0	285	5.91
0	298	4.17
0	308	3.04
1.62	298	4.18
3.25	298	4.17
6.57	280	6.64
6.57	285	5.73
6.57	298	4.01
6.57	308	3.09
6.57	317	2.31
6.57	328	1.76
9.82	298	4.62
12.78	280	9.01
12.78	285	7.63
12.78	298	5.30
12.78	308	4.13
12.78	317	3.22
12.78	328	2.62

Table II. Solubility Data for the Acetylene-2-Butyne-1,4-diol-Water System

concn of 2-butyne-1,4-diol, 10^3X, g-mol cm^{-3}	temp, K	solubility, 10^5S, g-mol cm^{-3} atm^{-1}
3.0	298	4.26
4.9	280	8.53
4.9	285	6.85
4.9	298	4.77
4.9	308	3.76
4.9	317	3.00
4.9	328	2.38
8.8	298	6.01
9.2	285	9.60
9.2	298	6.29
9.2	308	5.05
9.2	317	4.05
9.2	328	3.14

run started by switching the stirrer on. Volume of gas absorbed was recorded at different time intervals. After a few minutes, absorption of acetylene stopped as the solution became saturated. The total volume of gas absorbed gives directly the solubility in the volume of solution used. Necessary corrections for conversion of volume measured to STP and the vapour pressure of solution were made. For each condition, the experiments were carried out in triplicate to ensure reproducibility. The solubility value was taken as an average of these three values.

Results and Discussion

Solubility data for acetylene–water, acetylene–formaldehyde–water, and acetylene–2-butyne-1,4-diol–water systems were collected by a procedure described in earlier sections. The concentrations of formaldehyde and 2-butyne-1,4-diol were varied from 0 to 12.48 M and 0 to 9.2 M, respectively, while the temperature range investigated was 7–55 °C. The solubility data obtained for these systems are presented in Tables I and II. The values of S have been expressed as g-mol (cm^3 of solution)$^{-1}$ atm^{-1}. The data were corrected for the vapor pressure of the solution on the basis of Henry's law.

Though solubility of acetylene in water has been studied (*4*, *5*), the data on this system were reinvestigated to ensure the suitability of the apparatus. As may be noted from Figure 2 the values of solubility for the acetylene–water system determined in this work agree reasonably well with those reported in the literature. Though at some points the difference between our data and the literature values is about 10–11%, such differences are allowable in the experimental results of two groups. As far as our data are concerned, each experiment was repeated three times to ensure reproducibility. The maximum experimental error

Table III. Results of Regression Analysis

system	a	b	c	heat of dissolution $-\Delta H$, kcal g-mol^{-1}	std dev in S, σ
acetylene-formaldehyde-water	−16.0194	2.4559×10^3	0.472 47	4.91	8.38×10^{-7}
acetylene-2-butyne-1,4-diol-water	−15.7430	2.3851×10^3	0.408 65	4.77	1.99×10^{-6}

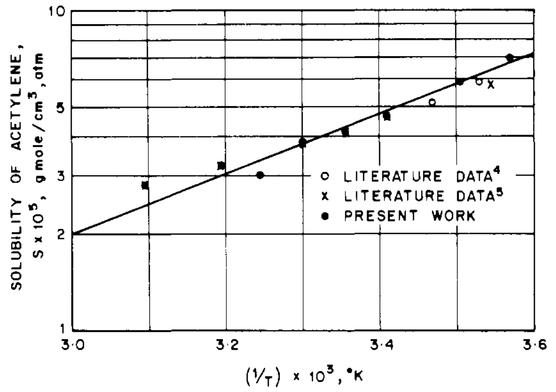

Figure 2. Temperature dependence of solubility of acetylene. Comparison between present work and literature data (*4*).

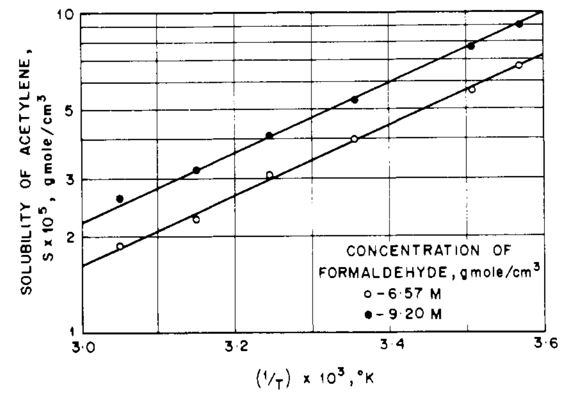

Figure 3. Temperature dependence of solubility of acetylene in formaldehyde solutions.

was found to be less than 4%.

Effect of Formaldehyde Concentration. From the solubility data presented in Table I, it may be noted that up to a formaldehyde concentration of 6.57 M, the solubility of acetylene was the same as in pure water, while beyond 6.57 M formaldehyde concentration the solubility increased with increase in concentration. When the concentration was increased from 6.57 to 12.78 M (a factor of 2), the solubility increased by about 32% at 298 K.

Effect of 2-Butyne-1,4-diol Concentration. In the case of the acetylene-2-butyne-1,4-diol-water system also the solubility was found to be unaffected up to 3 M concentration, but beyond 3.0 M 2-butyne-1,4-diol concentration, the solubility increased significantly with increase in the concentration. In this case the solubility values increased by about 48%, when the concentration was increased from 3.0 to 9.2 M (a factor of 3).

Effect of Temperature. The influence of temperature on the solubility of acetylene for formaldehyde-water and 2-butyne-1,4-diol-water systems is shown in Figures 3 and 4 as plots of ln S vs. $1/T$. As expected, the solubility was found to be a mild function of temperature. From the Arrhenius type of plots in Figures 2-4, the temperature-independent heat of solution, $-\Delta H$ (kcal g-mol^{-1}), was calculated. The values of $-\Delta H$ obtained for acetylene-water, acetylene-formaldehyde-water, and acetylene-2-butyne-1,4-diol-water systems were 4.31, 4.93, and 4.79, kcal g-mol^{-1}, respectively.

Correlation of Data. It is convenient to have a single equation from which solubility at a required temperature and concentration could be predicted. Therefore, the data in Tables I and II were correlated by using

$$\ln S = a + b/T + c \ln X \qquad (1)$$

where S represents the solubility of acetylene, g-mol cm^{-3} atm^{-1}, T is the temperature, K, X is the concentration of formaldehyde or 2-butyne-1,4-diol, g-mole cm^{-3}, and a, b, and c are constants. In order to obtain the best fit, we carried out regression analysis. For correlation purposes, data beyond 6.57 M formaldehyde and 3.0 M 2-butyne-1,4-diol concentrations were used, as below these concentrations the solubility is not concentration dependent. The values of the constants a, b, and c and the standard deviation σ (in solubility, S) are presented in Table III. The value of constant "b" is equal to the quantity $-\Delta H/R$, from which the average values of $-\Delta H$, the heat of solution, were

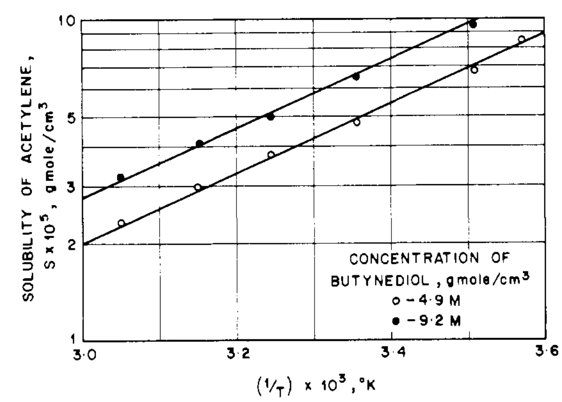

Figure 4. Temperature dependence of solubility of acetylene in 2-butyne-1,4-diol solutions.

obtained. These values compare well with those obtained graphically, from Figures 3 and 4.

Glossary

a	constant in eq 1
b	$-\Delta H/R$, constant in eq 1
c	constant in eq 1
R	gas constant, kcal g-mol^{-1} K
S	solubility of acetylene, g-mol cm^{-3} atm^{-1}
T	temperature, K
X	concentration of formaldehyde or 2-butyne-1,4-diol in water, g-mol cm^{-3}
$-\Delta H$	temperature-independent heat of solution, kcal g-mol^{-1}

Literature Cited

(1) Copenhaver, J. W., Bigelow, M. H., "Acetylene and Carbon Monoxide Chemistry", Reinhold, New York, 1949, p 98.
(2) Kale, S. S., Chaudhari, R. V., Paper presented at 4th National Symposium on Catalysis at Bombay, Dec 1978.
(3) Walker, J. F., "Formaldehyde", 3rd ed, Reinhold, New York, London, 1964, pp 485-97.
(4) Miller, S. A., "Acetylene: Its Properties and Uses", Vol. I, Ernest Benn Ltd., London, 1965, p 74.
(5) Wilhem, E., Battino, R., Wilcock, R. J., *Chem. Rev.*, **77**, 219 (1977).

Received for review March 13, 1979. Accepted December 27, 1979.