THE SOLUBILITIES OF COMPRESSED ACETYLENE GAS IN LIQUIDS, III

The Solubility of Compressed Acetylene Gas in Benzene*

By Ryo Kiyama and Hiroyuki Hiraoka

Introduction

The authors have previously reported the solubilities of compressed acethylene gas in water[1] and in methanol[2]. According to the measurements already published, the solubility of acetylene in benzene at one atmospheric pressure is fairly small as compared with that in the ideal solution and shows a positive deviation from Raoult's law, though the solutions with such nonpolar solvents as benzene may be practically assumed[4] to be nearly ideal**. In the present paper the solubility of acethylene in benzene in the range of pressure 5 to 30 kg/cm^2 and that of temperature 10 to 40°C, which have been never measured, is reported. From the same reason as in the case of methanol, the solvent, one can not consider the fugacity of acetylene in benzene as the function of the mole fraction of acetylene or the heat of solution only from the values of the solubility as the function of the total pressure. Nevertheless a positive deviation from Raoult's law could be found at each temperature in the solution of acetylene in benzene up to the maximum concentration in the present study, when it is assumed that the vapor pressure of benzene could be neglected as it is very low in comparison with the partial pressure of acetylene. And this deviation could be fairly well explained on the basis of the theory of regular solutions with the Flory-Huggins entropy correction arising from the difference of the molal volume of two substances.

Experimentals

Materials Acetylene gas is prepared with calcium carbide, its purity being 99.5~99.6% similarly in the previous researches. Benzene (extra pure reagent) is fractionated by distillation, after refluxing with metallic sodium for several hours and a portion with boiling point 80.0~80.2°C (760 mmHg) is taken, its density at 15°C

* *This investigation has been done by H. Hiraoka, being in the postgraduate course, under the direction of Prof. R. Kiyama.*

** The mole fraction of acetylene 208×10^{-4} is calculated in the ideal solution and 176×10^{-4} found in benzene at 25°C and 1 atm.

1) H. Hiraoka, *This Journal*, 24, 13 (1954)
2) R. Kiyama and H. Hiraoka, *ibid.*, 25, 16 (1955)
3) J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **17**, 125 (1931)
4) A. C. Mckinnis, *Ind. Eng. Chem.*, 47, 850 (1955)

being 0.88318.

Apparatus and experimental procedures The apparatus used and the experimental procedures are all the same as those described in the previous reports except that the rubber tube connecting the burette system with the high pressure apparatus has been replaced with a polyethylene tube.

Results

The vapor pressure[5] and density[6] of pure benzene at each temperature necessary for the calculation of the solubility, are taken from International Critical Tables and the solubility of acetylene in benzene at one atmospheric pressure and the coefficients of dilatation by absorption of acetylene in benzene are taken from the data[3] previously mentioned.

The results are given in Tables 1 and 2, the mole fraction of acetylene being denoted by N_2, and the number of cc of acetylene (S. T. P.) contained in 1 cc of benzene denoted by γ, respectively. In Fig. 1, in which the mole fraction of acetylene is plotted against the total pressure, it is observed that the mole fraction of acetylene is proportional to the total pressure up to about 10 kg/cm^2, and under higher pressures the deviation from this proportionality is found and the solubility becomes more and more larger than that obtained from this relation. Within the temperature range of the present investigation a linear relationship exists between the logarithm of the mole

Table 1 Solubility of acetylene in benzene
(mole fraction of acetylene, N_2)

Temp., °C / Press., kg/cm^2	10	20	30	40
1.033*	0.02280	0.01889	0.01587	0.01342
5	0.1220	0.1020	0.08013	0.06616
10	0.2460	0.1963	0.1633	0.1443
20	0.5431	0.4273	0.3653	0.3027
30		0.7280	0.6250	0.5431

* values of J. Horiuti[3]

Table 2 Solubility of acetylene in benzene
(cc-C_2H_2/cc-C_6H_6, γ)

Temp., °C / Press., kg/cm^2	10	20	30	40
1.033*	5.966	4.846	4.008	3.357
5	35.15	28.60	21.68	17.44
10	82.45	69.33	48.62	41.53
20	300.7	189.0	183.3	106.8
30		838.0	407.0	292.3

* values of J. Horiuti[3]

5) *Inter. Crit. Tables*, 3, p. 221
6) *ibid.*, 3, p. 29

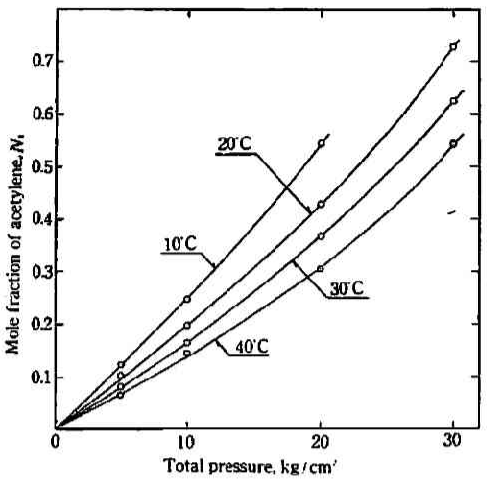

Fig. 1 Solubility of acetylene in benzene as function of total pressure

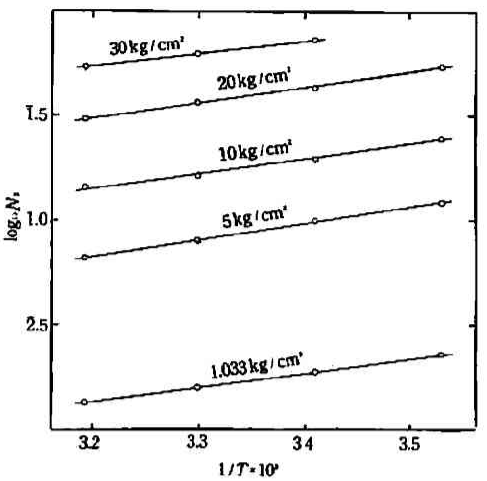

Fig. 2 Logarithm of mole fraction of acetylene plotted against reciprocal of absolute temperature

fraction of acetylene and the reciprocal of absolute temperature at each pressure and these straight lines have almost the same slopes (Fig. 2). In Fig. 2, the values at 1.033kg/cm² are obtained by converting the solubility of acetylene given in Ostwald's coefficients to the mole fractions, taking account of the dilatation by the absorption of acetylene in benzene.

Considerations

Now, one can not consider the fugacity of acetylene as the function of the mole fraction or the heat of solution in a strict manner, because no knowledge about the fugacity or the activity of acetylene in benzene could be got only from the values of the solubility as the function of the total pressure. Nevertheless, with the assumption that the vapor pressure of benzene might be neglected as it is very low in comparison with the partial pressure of acetylene, the fugacity of acetylene in benzene may be regarded as equal to that of acetylene in the gaseous phase, which is assumed to be pure acetylene.

Fig. 3 indicates the relation between the mole fraction of acetylene in benzene and the fugacity obtained from the assumption mentioned above. The fugacity at $N_2=1$ is that of pure liquid acetylene in equilibrium with its vapor at each temperature, calculated by graphical integration using the state diagram[7] and given in Table 3. The value at 40°C is the fugacity of the hypothetical liquid acetylene, the vapor pressure of which is obtained by extrapolating the plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature, which shows practically a straight line right up to the critical point according to the Clausius-Clapeyron's equation.

7) R. Kiyama, T. Ikegami and K. Inoue, *This Journal*, **21**, 58 (1951)

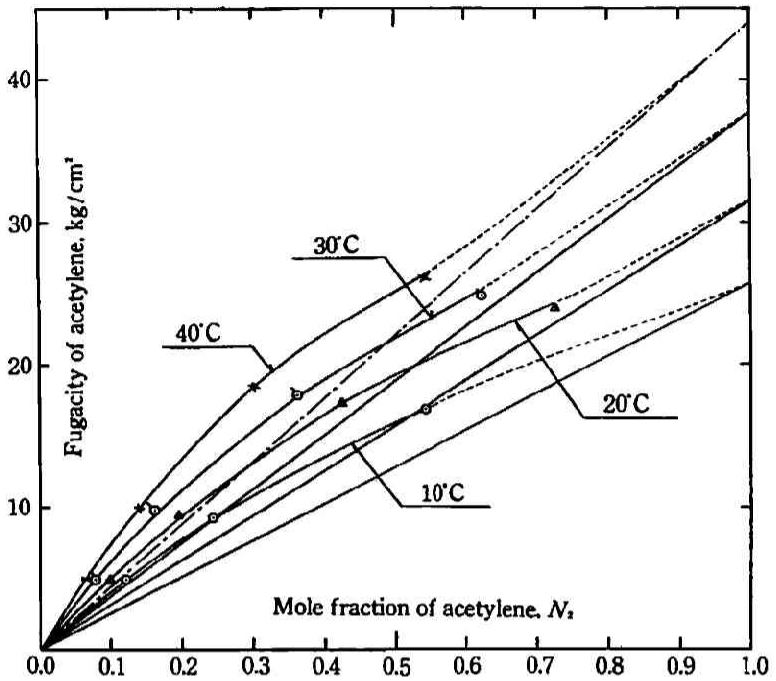

Fig. 3 Fugacity of acetylene plotted against mole fraction of acetylene

Table 3 Fugacity of acetylene

Temperature, °C	0	10	20	30	40
Vapor pressure, atm	26.3	33.9	43.1	54.1	(67.0)
Fugacity, atm	20.9	25.6	31.4	37.7	(44.1)

Hildebrand pointed out that such a fictitious value could be used to define an ideal gas solubility, even above the critical temperature of the gas. As the fugacities of acetylene gas at 40°C, the authors have used the following values, which are not given in the previous report,

$$f_{10}=9.698,\quad f_{20}=18.46,\quad f_{30}=26.13,\quad f_{40}=32.67,\quad f_{50}=38.08,\quad f_{60}=42.19$$

where f_x is the fugacity (kg/cm²) of acetylene gas at the pressure $x$kg/cm² at 40°C. In Fig. 3, a positive deviation from Raoult's law is found at each temperature and with the increase of temperature the experimental line approaches the straight line of Raoult's law, especially at a concentrated part of acetylene.

A positive deviation from Raoult's law is, in general, favored by (1) differences in the internal pressure and in the molal volume (2) dissimilarities in the polarity (3) the association of one or both of two substances. Among these the difference in the internal pressure and in the molal volume may be considered to be most influential, for the others could not exist in such a binary solution as benzene+acetylene.

According to the theory of regular solutions with the Flory-Huggins entropy cor-

rection taking account of the disparity in molal volumes, Equation (1) is obtained[8],

$$\ln\frac{f_2}{f^0_2}=\ln\varphi_2+\varphi_1\left(1-\frac{V_2}{V_1}\right)+\frac{V_2\varphi_1^2(\delta_2-\delta_1)^2}{RT}, \qquad (1)$$

where f denotes the fugacity, f^0 the fugacity in the pure state, φ's the volume fractions, v's the molal volumes of the liquids. The subscript 1 refers to benzene and the subscript 2 to acetylene. The solubility parameters, δ's, are calculated from Equation (2),

$$\delta=\left\{\frac{(\Delta H_{app}{}^V-RT)Z}{V^L}\right\}^{1/2}, \qquad (2)$$

where Z denotes the compressibility factor, V^L the molal volume of the liquid, and $\Delta H_{app}{}^V$ the heat of vaporization calculated from the temperature dependence of the vapor pressure by means of the Clausius-Clapeyron equation, which is the true heat of vaporization only at vapor pressures low enough that the vapor is ideal. The results of the application of Equation (1) for the binary solution of acetylene+benzene at 10°C is given by the dotted line in Fig. 4. The assignment of values in Equation (1) is as

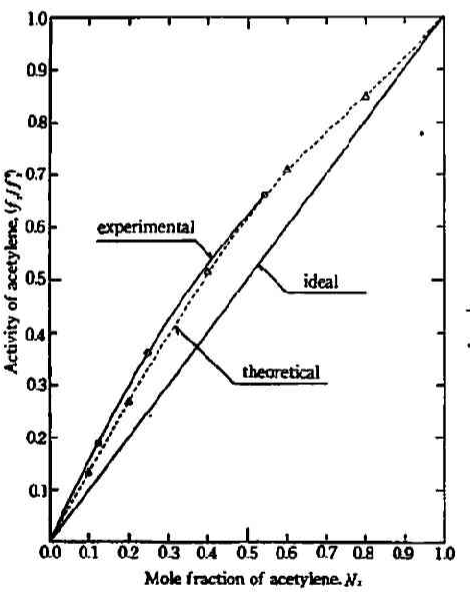

Fig. 4 Theoretical and experimental curves representing the relations between the mole fraction and the activity at 10°C

—○— experimental curve

·····△····· theoretical curve

follows: $V_1=87.77$ ml, $V_2=59.89$ ml, $\Delta H_{app}{}^V=3859$ cal/mole. $\delta_1=9.31$, with $Z=1$ in Equation (2). For the solubility parameter of acetylene the authors used the corresponding value from 7.46 to 5.94 to the change from $Z=1.000$ at zero pressure to $Z=0.6331$ at 33.9atm, the vapor pressure of acetylene at 10°C. Such a change in the value of the solubility parameter is important in the considerations of the solutions in which compressed gases are dissolved.

The theoretical line conforms reasonably well with the experimental line, when

8) *cf.* J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolyte*, 3rd Ed. (1950) p. 131.

one considers the approximations involved in Equation (1)——the assumption of spherical, nonpolar molecules, the simplication of the interaction terms between molecules, the negligence of the volume change on mixing and so on ——and the disregard for the vapor pressure of benzene in the calculation of the fugacity of acetylene. And it may be reasonable that the experimental line deviates more positively than the theoretical line from Raoult's law, for in the calculation of the fugacity of acetylene in benzene the authors assume that the gaseous phase in equilibrium with the liquid phase is pure acetylene.

The authors are indebted to the Department of Education for the Grant in Aid for the Fundamental Scientific Individual Research.

The Laboratory of Physical Chemistry,
Kyoto University