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THE SOLUBILITIES OF COMPRESSED ACETYLENE GAS IN LIQUIDS, IV

The Solubility of Compressed Acetylene Gas in Tetrahydrofuran*

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Introduction

In the previous papers, the authors reported the solubilities of compressed acetylene gas in water1), methanol2) and benzene3) and found that the solubility of acetylene in water at high pressures deviates negatively from Henry's law in the from $N_2=kP$, where N_2 is the mole fraction of acetylene, P the partial pressure of acetylene and k a constant and the solubility is nearly proportional to the fugacity of acetylene, while the solubilities in methanol and in benzene at high pressures deviate positively from Henry's law and moreover the solution of benzene shows the positive deviation from Raoult's law and this deviation could be well explained on the basis of the theory of regular solutions with the Flory-Huggins entropy correction arising from the difference in the molal volumes of the two substances. In the present paper, the solubility of acetylene in tetrahydrofuran having an electronegative oxygen atom in the molecule, a donor solvent for acetylene, in the range of temperature from 0 to 30°C and up to pressure 30 kg/cm², which has been never measured, is reported and rather qualitative considerations upon the characteristics of acetylene solutions are given.

Experimentals

Tetrahydrofuran used as the solvent is fractionated by distillation, after refluxing with metallic sodium for several hours and a portion with boiling point 66.1~66.3°C (760 mmHg) is taken, and its vapor pressure measured with an isoteniscope in the range of 60 to 760 mmHg and its density from 5 to 30°C are represented by Eqs. (1) and (2), respectively,

$$d_t=0.9079-9.93\times10^{-4}t-1.6\times10^{-6}t^2 \quad , \qquad (1)$$

$$\log_{10} P_t=\frac{-1.022\times10^{-3}}{t+205}+5.635 \quad , \qquad (2)$$

where P_t is in mmHg and t in degrees centigrade.

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

1) H. Hiraoka, *This journal*, **24**, 13 (1954)

2) R. Kiyama and H. Hiraoka, *ibid.*, **25**, 16 (1955)

3) R. Kiyama and H. Hiraoka, *ibid.*, **25**, 52 (1955)

Acetylene used as the solute and the experimental procedures for the present measurements are all the same as those described in the previous reports.

Results

The vapor pressure and density of tetrahydrofuran at each temperature used in the calculation of the solubility are represented by Eqs. (1) and (2) and the coefficients of dilatation by the absorption of acetylene in tetrahydrofuran are assumed to have the same value as in acetone[4] because the data in tetrahydrofuran are lacking and the difference among the values in the other solvents is comparatively small if the solvents are like one another,* and the correction of the solubility due to the dilatation is small.

Table 1 Solubility of acetylene in tetrahydrofuran at one atmosphere

Temperature, °C	Bunsen's coeff.
5	30.1
10	26.0
15	22.0
20	19.5
25	17.3

The solubility of acetylene in tetrahydrofuran at one atmospheric pressure is given in Table 1 and represented by Eq. (3),

$$\log_{10} N_2 = \frac{8.857 \times 10^2}{T} - 4.155 \quad , \qquad (3)$$

where N_2 denotes the mole fraction of acetylene and T the absolute temperature.

In Tables 2 and 3, the solubility of compressed acetylene gas in tetrahydrofuran is given in the mole fraction of acetylene and the numbers of cc of acetylene (*S. T. P.*)

Table 2 Solubility of acetylene in tetrahydrofuran

(mole fraction of acetylene, N_2)

Temp. °C / Press., kg/cm²	0	10	20	30
5	0.341	0.287	0.231	0.192
10	0.514	0.439	0.369	0.323
15		—	0.491	0.433
20		0.691	0.595	0.532
25			0.704	0.613

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* This will be confirmed in the following paper in which the partial molal volumes of acetylene in various solvents will be reported.

4) J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, 17, 125 (1931)

Table 3 Solubility of acetylene in tetrahydrofuran
(cc-C_2H_2/cc-C_4H_8O)

Press., kg/cm² \ Temp., °C	0	10	20	30
5	145	112	82.1	64.2
10	296	217	160	129
15		—	264	207
20		617	402	307
25			649	429

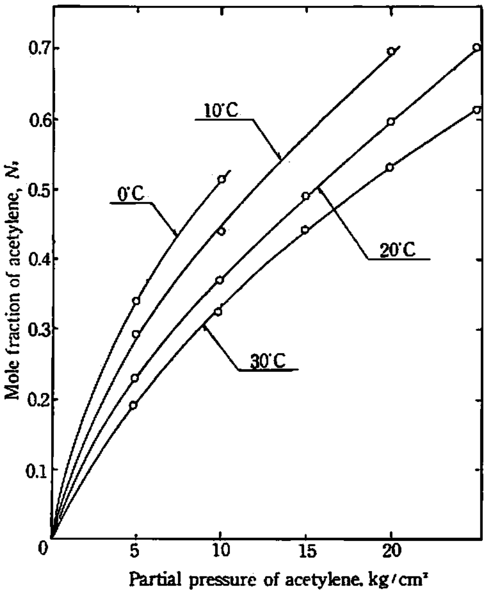

Fig. 1 Solubility of acetylene in tetrahydrofuran as function of partial pressure of acetylene

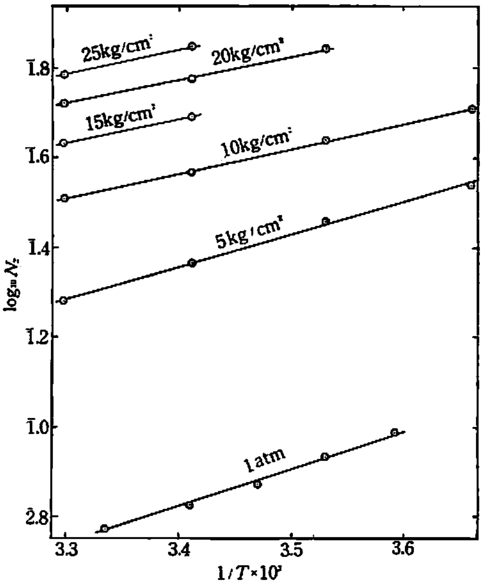

Fig. 2 Logarithm of mole fraction of acetylene plotted against reciprocal of absolute temperature

contained in 1 cc of tetrahydrofuran, respectively. In Fig. 1, in which the mole fraction of acetylene is plotted against the partial pressure of acetylene, it is observed that the solubility at high pressures deviates negatively from Henry's law in the form $N_2=kP$ and Fig. 2 shows that a nearly linear relationship exists between the logarithm of the mole fraction of acetylene and the reciprocal of the absolute temperature at each pressure within the temperature range of the present investigation. The conversion of the total pressure to the partial pressure of acetylene has been made using Dalton's law, and the mole fraction of tetrahydrofuran in the gaseous phase calculated according to the method developed by Robin *et al.*, which is described later.

Considerations

The authors have measured the solubilities of acetylene in water, methanol, benzene and tetrahydrofuran and these solubilities are classified into two cases in view of the effect of the partial pressure of acetylene. One is the case in which the solubility at high pressures deviates positively from Henry's law and the other the case in which the solubility deviates negatively. The solubilities in methanol and in benzene belong to the former and those in water and in tetrahydrofuran to the latter, as is seen from Fig. 3 in which the mole fraction of acetylene is plotted against the partial pressure of acetylene. In the latter case, it is notable that the solubility in water is exceptionally low and proportional to the fugacity of acetylene and the solubility in tetrahydrofuran is the highest among those in these solvents used and fifty times as high as the mole fraction of acetylene in water at 20°C and 20 kg/cm^2. It may be considered that the solubility of acetylene in alcohol or in nonpolar solvents in general belongs to the former and the solubility of acetylene in donor solvents or in water to the latter, when the solubility is represented by the mole fraction of acetylene.

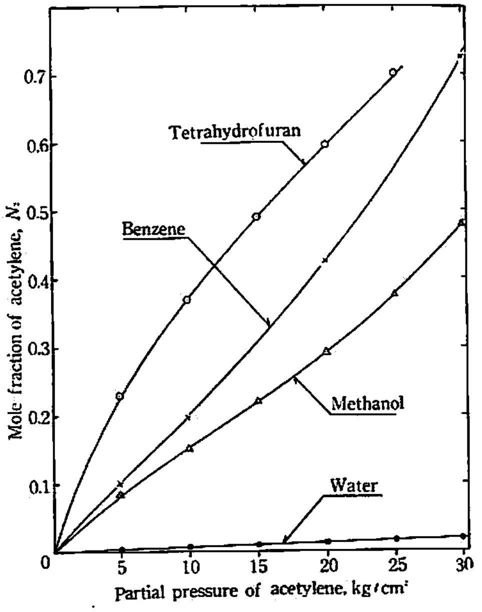

Fig. 3 Solubility of acetylene as function of partial pressure of acetylene at 20°C

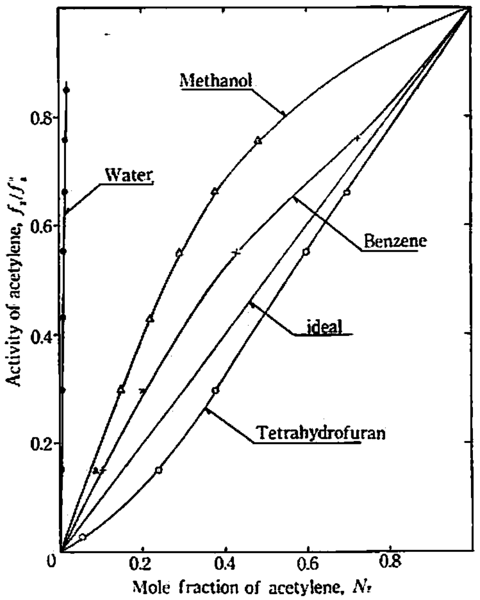

Fig. 4. Activity of acetylene plotted against mole fraction of acetylene at 20°C

Now, pure liquid acetylene in equilibrium with its vapor at each temperature is chosen as the standard state of acetylene in the liquid solution, then the activity of acetylene in the liquid solution in equilibrium with the gaseous phase is equal to the ratio of the fugacity of acetylene in the solution to that in the pure liquid state. The fugacity of pure acetylene is already reported and the concentration of the liquid solvent in the gaseous phase necessary to the calculation of the fugacity of acetylene in solutions is assumed to be approximately computed by Eq. (4) according to Robin *et al.*[5],

$$\log\left(\frac{m}{m_0}\right)=(A+B/T)\rho \quad , \qquad (4)$$

where m is the mass of the liquid solvent per 1 cc of the gaseous phase of density ρ in Amagat unit and m_0 the mass of the liquid solvent contained in 1 cc of the gaseous phase in the absence of the compressed gas. The constants in Eq. (4) are shown in the table.

System	A	B
acetylene-water	−0.00187	2.45
acetylene-methanol	−0.00234	2.01
acetylene-benzene	−0.00544	5.75
acetylene-tetrahydrofuran	0.00160	

In the last system, acetylene-tetrahydrofuran, the first term A on the right hand side of Eq. (4) contains only the contribution by the Poynting effect, and the second term is taken into no account because the appropriate physical constants of tetrahydrofuran necessary to the calculation are unavailable. Then the fugacity of acetylene in solutions in equilibrium with the gaseous phase is calculated as an approximation using Lewis-Randall's law, $f_2=f_2^0N_2$, where f_2 is the fugacity of acetylene in the solution and f_2^0 the fugacity in the pure state. The difference between the value of the fugacity thus obtained and the value under the assumption that the gaseous phase is pure acetylene is considerable at high temperatures and low pressures, but the difference is only slight at low temperatures and high pressures.

Fig. 4, in which the activity of acetylene in each solution at 20°C is plotted against the mole fraction of acetylene, shows that the positive deviations from Raoult's law are found in the solution of acetylene in water, methanol and benzene, whereas the negative deviation in the solution of acetylene in tetrahydrofuran. In the discussion of the solutions of compressed gases, the change of free energy or activity with pressure must be taken into account and this change is related by the well known thermodynamic equation to the partial molal volume of the solute in solutions. In the following paper the authors will report on the measurements of the partial molal volume of acetylene in the wide range of concentration in the various solvents. So, in the present paper qualitative considerations about the characteristics of acetylene solutions may be rather given in the following.

Acetylene-water system

As mentioned previously, the solutions of acetylene in water, alcohol and nonpolar solvents, such as benzene, deviate positively from Raoult's law. Among them, aqueous

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[5] S. Robin et B. Vodar, *J. Phys. et Rad.*, **13**, 264 (1952)

solution shows the largest positive deviation and Fig. 5 indicates that the isotherms of the activity against the mole fraction at 20°C and 30°C are linear and nearly coincide with each other but the activity at a low temperature gradually decreases from the values at 20°C and 30°C. These indicate that the heat of solution of liquid acetylene in water is negative, that is, exothermic and the excess partial molal entropy of solution has a large negative value. The assumption[6], [7] that the rare gases and hydrocarbon gases form "iceberg" when they dissolve in cold water and that those molecules in solution may be surrounded by oriented cages of water molecules, gives a fine interpretation for the characteristics of aqueous solution of acetylene and it is observed that the isotherms at temperatures higher than the critical temperature of the hydrate of acetylene, which is obtained from the cross point of the vapor pressure of acetylene and that of the gas hydrate and is equal to 16°C[8], would nearly coincide, whereas the isotherms at lower temperatures are drawn lower with decreasing temperatures and from this the partial molal heat capacity of acetylene in aqueous solution is supposed to be large at lower temperatures.

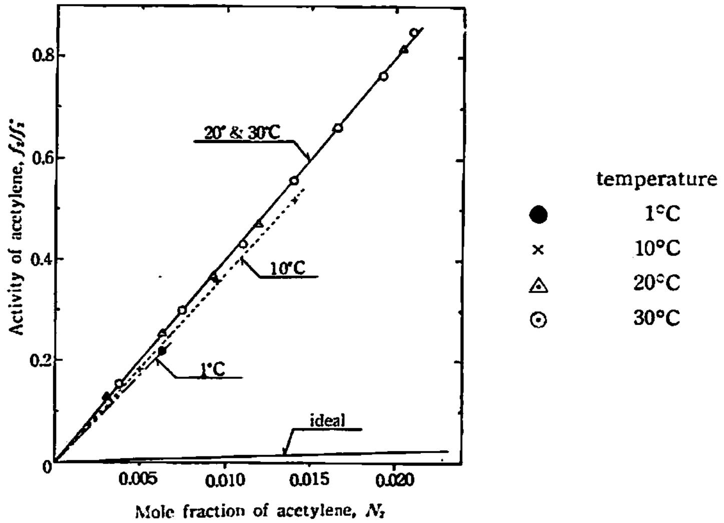

Fig. 5 Activity of acetylene in water plotted against mole fraction of acetylene

Acetylene-methanol system

Acetylene-methanol system shows a positive deviation from Raoult's law, as a net result of various factor, the association of methanol, the difference in the internal pressures of the two substances, the interaction of methanol and acetylene, the difference in the molal volumes of the two substances and so on. The temperature

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6) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 13, 507 (1945)
7) W. F. Claussen and M. F. Polglase, *J. Am. Chem. Soc.*, 74, 4817 (1952)
8) M. V. Stackelberg und H. R. Müller, *Zeit. Electrochemie*, 58, 25 (1954)

coefficient of the activity of acetylene in methanol is positive, as shown in Fig. 6, so that the heat of solution of liquid acetylene in methanol is negative in accordance with Mcintosh's observation[9] of the formation of a crystalline compound of acetylene and alcohol at low temperatures.

Acetylene-benzene system

In the previous paper, the authors reported that the solution of acetylene in benzene shows a positive deviation from Raoult's law and this deviation could be explained on the basis of the theory of regular solutions with the Flory-Huggins entropy corrections arising from the differences in the molal volumes of the two substances. Moreover the temperature coefficient of the activity of acetylene is negative, so that the heat of solution of liquid acetylene in benzene is positive, that is, endothermic in accordance with the theory of regular solutions, although the heat of solution of gaseous acetylene in benzene is of course exothermic owing to the condensation of the gas. It may be considered that this interpretation may be applicable to other solutions of acetylene in nonpolar solvents.

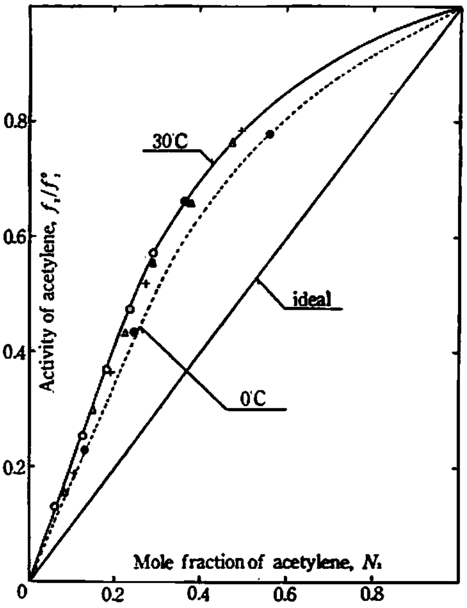

Fig. 6 Activity of acetylene in methanol plotted against mole fraction of acetylene

	temperature
●	0°C
×	10°C
△	20°C
⊙	30°C

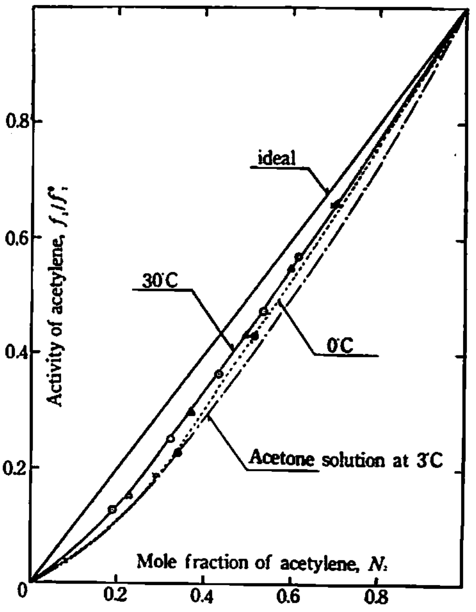

Fig. 7 Activity of acetylene in tetrahydrofuran plotted against mole fraction of acetylene

	temperature
●	0°C
×	10°C
▷	20°C
⊙	30°C

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[9] D. Mcintosh, *J. Phys. Chem.*, 11, 306 (1907)

Acetylene-tetrahydrofuran system

Tetrahydrofuran has an electronegative oxygen atom in the carbon chain of the molecule which has electrons that are available for hydrogen bond formation with the proton of acetylene. Studies on the solubility of acetylene in such a donor solvent having an active center have been made extensively from the technical point of view, but those under high pressures are comparatively few. The solubility of acetylene in acetone measured by Hölemann *et al.*[10] changes in the same manner as in tetrahydrofuran with pressure.

Fig. 7, in which the activity of acetylene is plotted against the mole fraction of acetylene, shows that the negative deviation from Raoult's law in the solution of acetylene in tetrahydrofuran is slightly smaller than that in the solution of acetone obtained from the data by Hölemann *et al.* and the temperature coefficients of the activity of acetylene in both solvents are positive, indicating that the heats of solution in such donor solvents are negative, that is, exothermic and the strong specific interaction between acetylene and donor solvent molecule may be expected in accordance with the assumption of hydrogen bond formation between the electronegative atom in the donor solvent and the proton of acetylene.

Part of the present measurements has been done by Mr. N. Yoshida.

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[10] P. Hölemann und R. Hasselmann. *Chem. Ing. Technik,* 25, 466 (1953)