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PARTIAL MOLAL VOLUMES OF COMPRESSED ACETYLENE GAS IN LIQUIDS*

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Introduction

As a part of the investigations on the solution in which acetylene gas is dissolved, the authors have already reported its solubilities in several liquids[1]. In the present investigation, the partial molal volumes of compressed acetylene gas indispensable in the theoretical study of the solution are measured and the thermodynamic considerations on the solution are given.

The dilatation of the solvent caused by the dissolution of the gas has already been measured by many investigators[2], and Hildebrand *et al.*[3] made a summary of the results in the term of the partial molal volumes of the gases. Many of these investigations, however, were done at an atmospheric pressure, so that the concentration of the dissolved gas, such as acetylene, in the solution is limited within the very small value on account of their low solubility at an atmospheric pressure. The measurements of the partial molal volume of the compressed gases in liquids are necessary for the investigation on the gaseous solutions covering a wide range of the concentation. But the measurements of this kind are very few, and for instance, have been done on liquid ammonia-hydrogen system by Wiebe *et al.*[4] and on hydrogen and nirogen in benzene and methanol and on hydrogen, nitrogen and methane in liquid ammonia by Krichevskii *et al.*[5]. Wiebe *et al.* obtained the partial molal volumes from the concentration of the solution contained in the steel tube with a valve at each end, the volume of which is measured by fitting it with hydrogen at 100 and 200 atm. To the authors' regret the papers of Krichevskii *et al.* are not available. Newitt *et al.*[6] had also measured the specific volume of the system ethane-propylene by visual observation. The authors devised the new apparatus, different

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

1) H. Hiraoka, *This Journal*, 24, 13 (1944)
R. Kiyama and H. Hiraoka, *ibid.*, 25, 16 (1955), 25, 52 (1955), 26, 1 (1956)

2) *cf.* J. Horiuchi, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, 17, 125 (1931)

3) J. H. Hildebrand and R. Scott, *The Solubility of Nonelectrolytes*, Reinhold Publishing Co., 3rd Ed., p. 247 (1950)

4) R. Wiebe and T. H. Tremearne, *J. Am. Chem. Soc.*, 57, 2601 (1935)

5) I. R. Krichevskii and G. D. Efremova, *Zhur. Fiz. Khim.*, 22, 116 (1948), 26, 4890 (1952), 26, 1117 (1952), 27, 1682 (1953)
cf. Chem. Abs., 43, 469 (1949), 46, 4890 (1952), 49, 2828 (1954), 49, 6677 (1953)

6) H. Lu, C. M. Newitt and M. Ruhemann, *Proc. Roy. Soc.*, A178, 506 (1941)

from the apparatus of Wiebe *et al.* and Newitt *et al.*, applicable to the case of compressed gas as solute, standing on the same principle with the dilatometer method, which is used for the measurement at an atmospheric pressure. The principle of the dilatometer method is the measurement of the dilatation of the solvent when it absorbs the gas, the volume of which is also measured. With this newly devised apparatus the authors measured the partial molal volume of each component of the acetylene solutions, covering a wide range of the concentration, the solvents of which are water, benzene, acetone and methanol, and also measured the thermal expansion coefficients and the compressibility of the solution. Besides these measurements, the authors determined the solubility of acetylene from the pressure at which acetylene dissolved in the solution began to bubble when pressure was decreased little by little at constant temperature and compared the results with the solubility of acetylene previously published.

Experimentals

Materials Acetylene gas, methanol and benzene are all the same as those in the previous reports[1]. Acetone is collected from 56.1 to 56.3°C (760 mmHg) by distillation.

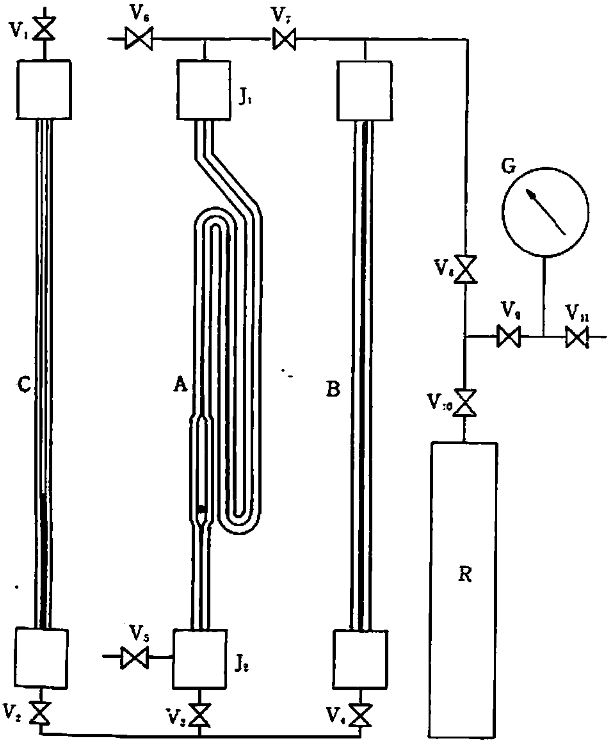

Fig. 1 Layout of the apparatus

A, B and C: glass tubes
J: glass-steel joint
G: Bourdon type pressure gauge
R: compressed air reservoir
V: high pressure valve

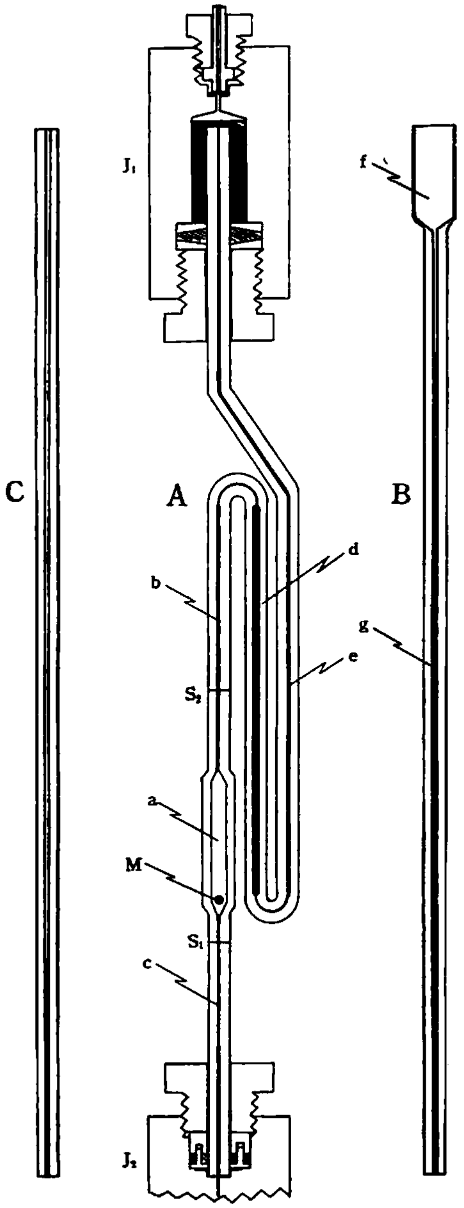

Fig. 2 Details of glass tubes and glass-steel joints.

Volumes of each part of glass tubes are as follows.

A tube	No. 1	No. 2
a(S_1 to S_2), ml	1.7214	1.5696
b, ml/cm	2.255×10^{-2}	0.800×10^{-2}
c, ml/cm	0.898×10^{-2}	1.225×10^{-2}
d(inner dia.), cm	0.3	0.3
e(inner dia.), cm	0.1	0.1

B tube	No. 1	No. 2	No. 3
f, ml	ca. 16	ca. 16	ca. 16
g, ml/cm	4.666×10^{-2}	4.020×10^{-2}	4.037×10^{-2}

C tube 4.874×10^{-2}ml/cm

Experimental apparatus and procedures The method used at an atmospheric pressure to measure the volume change of the solvent by the gas absorption may be classified as follows: 1) the pycnometer method, 2) the dilatometer method and 3) the hydrometer method. The apparatus applicable to the measurements under pressure, devised by the authors, belongs to the dilatometer method. Fig. 1 shows the layout of the pressure transmitting part of the apparatus. In Fig. 1, A, B and C are glass tubes. With A tube the dilatation by the absorption of the gas is measured and with B and C tubes the volume of the gas absorbed is measured. The details of these glass tubes and of the methods of glass-steel joints are shown in Fig. 2. Vs are high pressure valves, R the compressed air reservoir and G a Bourdon type pressure gauge graduated to 1.0 kg/cm², its maximum marked pressure being 50 kg/cm².

In the present investigation, two glass A tubes, No. 1 and 2, are used. The capacities of the a part from lower standard line S_1 to upper standard line S_2 are 1.7214 and 1.5696 ml at 10°C respectively. Every part of b and c of A tube is measured precisely and their capacities in ml/cm are respectively 2.255×10^{-2} and 0.800×10^{-2} on an average at b part and respectively 0.898×10^{-2} and 1.225×10^{-2} on an average at c part. The d part of A tube is about 0.3 cm in inner diameter and the e part about 0.1 cm in inner diameter. The capacities in ml/cm of g part of three B tubes used, No. 1, 2 and 3, are 4.666×10^{-2}, 4.020×10^{-2} and 4.037×10^{-2} respectively. The f part of B tube, which is about 16 ml in capacity and serves as a mercury reservoir, is put in the interior of the steel-glass joint similar to J_1. The lower steel tube joining A, B and C glass tubes is filled with mercury, its quantity being adjusted at the beginning of the experiment so that its heads in three tubes can be near the lower standard line S_1 in A tube, at the upper part in B tube and at the lower part in C tube at the same time. The A tube is filled with solvent in the following manner. The steel tube joined with J_1 above the A tube, is disconnected and mercury is introduced into A tube through V_5. After mercury fills A tube and the interior of J_1, the solvent is introduced into A tube through a glass capillary from the upper end of J_1, the head of mercury being lowered gradually. When an appropriate quantity of the solvent is introduced into A tube, mercury then follows the solvent from the upper end of J_1. In this way the solvent is placed between the upper and lower mercury as shown in Figs. 1 and 2, when the solvent is taken in the a part. If the quantity of the solvent thus taken is too much to measure the volume increase in the b part, the excess quantity of the solvent is discarded by the exchange with mercury in the interior of J_1, after the solvent is taken to the d and e parts by the lift of the lower mercury head following the introduction of the mercury into A tube through V_5. The volume of the solvent thus taken into the A tube is determined at each experimental temperature and pressure from the measurements of the heights of the upper and lower meniscus of the solvent, which are read to 1/100 cm by a cathetometer. The pressure within the apparatus is adjusted by the compressed air reservoir R and read by the gauge G. The very small volume change caused by the pressure which is exerted by the mercury on the solvent in A tube is corrected.

Compressed acetylene gas is reserved above mercury in C tube, which is surrounded by a water thermostat. After the temperature equilibrium is established in C tube, V_2, V_3 and V_4 are opened and three heads of the mercury filling the lower steel tube are balanced by the suitable choice of the pressure above mercury in A and B tubes so that the heads are near the lower standard line S_l, at the upper part in B tube and at the lower part in C tube, while V_7, V_8, and V_9 are opened. After the balance is kept between three columns of mercury in A, B and C tubes, V_2, V_3 and V_4 are closed and the pressure indicated by the pressure gauge G, the heights of mercury columns in A, B and C tubes, and the temperatures of the water thermostats surrounding A and C tubes are read off. The temperatures of the water thermostats are kept at constant near a room temperature until the following procedure of the absorption of the gas in the solution is finished. Then V_2 and V_4 are opened and the compressed acetylene gas is brought near the junction of A and B tubes by the discard of the compressed air from V_{11} and the subsequent decrease of the pressure above mercury in B tube, while mercury in B tube is raised into the f part. When acetylene gas is going to dissolve in the solvent, the contact surface of the solvent with the upper mercury in A tube is placed in the d part and the lower half of the a part is filled with mercury. After a quantity of acetylene gas is dissolved in the solution gradually, the mercury filling the lower half of the a part is brought back to the previous place by the compressed air from R and then V_3 is closed and then the mercury in the f part is sent back into C tube until the pressure of acetylene above mercury in C tube becomes equal to that before the absorption.

The quantity of acetylene gas absorbed can be calculated from the difference of the heights of mercury column in B tube at the temperature and pressure previously read off, with the correction due to the difference of the heights of mercury column in B and C tubes. And the correction for the occluded gas in the lower steel tube is also needed, because this occluded gas is compressed under the pressure higher than that above the mercury by the pressure difference caused by mercury column above it. The volume of the occluded gas is determined from the apparent increase of the volume of the mercury occupying the lower steel tube line.

After the absorption procedures just stated above is finished, the solution is stirred magnetically by a stirrer M and the temperature of the thermostat surrounding A tube is kept at an experimental temperature. After the temperature equilibrium is established, the heights of the upper and lower contact surfaces of the solution with mercury are read off by means of a cathetometer and the volume of the solution is measured. After the measurements of the volumes at one experimental temperature is finished, the temperature of the thermostat is changed and the volume of the solution is measured at the other temperature after the new thermal equilibrium is attained. In this way the isobaric thermal expansion of the solution at constant concentration is measured and moreover the isothermal compressibility of the solution at constant concentration may be determined. After all these measurements at one concentration is finished, the excess quantity of the solution is discarded in the interior of J_1 by the procedure stated before by introducing mercury into A tube from C tube and then the volume of the solution is measured and the next absorption of the gas is made. In this way the concentration of acetylene in the solution is increased continuously and the volume change of the solution by the absorption of the gas is measured at each concentration. Each experimental temperature is kept constant within the flactuation of ±0.02°C in the thermostat.

Now, the volume of the acetylene gas dissolved is measured at temperature T^0 K and at pressure P kg/cm , so that the mole numbers of acetylene dissolved may be calculated from the P-V-T data of acetylene already published7). In the dilute solution such as the aqueous solution of acetylene, the apparent molal volume of acetylene, which is equal to the volume increase of the solution by the absorption of one mole of acetylene, may be regarded as equal to the partial molal volume of acetylene. However for the other solutions this approximation is not correct and the authors give the experimental results in the term of the mean molal volume of the solution and then calculated the partial molal volume by the Bakhuis-Rooseboom method5).

For the purpose of ascertaining whether the concentration of the solution obtained by the above procedure is in accordance with the results of the solubility measurements already reported, the pressure at which acetylene dissolved in the solution begins to bubble at constant temperature, is measured from the gradual decrease of the pressure, while the solution is stirred by a stirrer M.

Experimental Results

The values of the densities of each pure solvent at an atmospheric pressure necessary for the calculation of the partial molal volume are taken from International Critical Tables and the P-V-T data of acetylene is taken from the calculated values by Din, which seems to be the most suitable in the range of pressure and temperature in the present investigation.

Table 1 Partial molal volume of acetylene in water $\overline{V}_2$ (ml), specific volume of water v_1 (ml) at 30 kg/cm^2 and compressibility β of water and aqueous solution of acetylene

Mole fraction of acetylene	0.000		0.0115		0.0159
Temperature °C	v_1	$\beta\times10^5$	$\overline{V}_2$	$\beta\times10^5$	$\overline{V}_2$
2	0.9986	4.1	38.9	—	—
10	0.9988	5.0	38.9	9.2	38.5
25	1.0014	—	40.0	—	—
40	1.0061	6.3	40.8	—	—

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7) J. Sameshima, *Bull. Chem. Soci., Japan*, 1, 41 (1926)
R. Kiyama, T. Ikegami and K. Inoue, *This Journal*, 21, 58 (1951)
F. Din, *Thermodynamic Functions of Gases*, Vol. 2 Butterworths Scientific Publications (1956)

8) *cf.* I. Prigogine and R. Defay, *Chemical Thermodynamics*, translated by D. H. Everett, Longmans Green and Co., p. 7 (1954)

Table 2 Mean molal volume (ml) of acetylene-benzene solution at 30 kg/cm^2

Mole fraction of acetylene	10°C	25°C	40°C
0.0000	87.61	89.17	90.72
0.0910	—	86.85	88.47
0.0737	84.79	86.35	—
0.1176	—	84.76	86.19
0.1994	79.91	81.55	—
0.2555	77.70	79.36	—
0.3121	75.60	77.29	78.90
0.3609	73.99	—	—
0.3614	—	75.73	77.56
0.4056	72.55	74.37	
0.4476	71.25	73.01	
0.4841	69.71	71.91	
0.5148	68.70		
0.5479	67.60		
0.5734	66.91		

Table 3 Mean molal volume (ml) of acetylene-acetone solution at 30 kg/cm^2

Mole fraction of acetylene	10°C	25°C	40°C
0.0000	72.30	73.75	75.40
0.0481	71.05	72.49	74.14
0.0949	—	71.32	—
0.1155	—	70.75	—
0.1500	68.30	69.90	71.54
0.1956	—	68.75	70.41
0.2238	—	68.10	—
0.2363	66.10	67.70	—
0.2780	65.17	66.80	—
0.3164	64.30	66.00	—
0.3557	63.50	65.23	67.02
0.3847	63.01	64.72	66.49
0.4209	62.40	64.15	
0.4330	62.21	63.96	

Water-acetylene system Experimental results for water-acetylene system are shown in Table 1, in which v_l is the specific volume of pure water at 30 kg/cm^2 and at each temperature, $\overline{V}_2$ the partial molal volume of acetylene dissolved at 30 kg/cm^2 and at each temperature and β the average compressibility of water and aqueous solution between 1 atm and 30 kg/cm^2. It is impossible to measure the volume of

Table 4 Mean molal volume (ml) of acetylene-methanol solution at 30 kg/cm^2

Mole fraction of acetylene	10°C	25°C	40°C
0.0000	39.98	40.59	41.43
0.0250	40.18	40.82	41.83
0.0691	40.58	—	—
0.1068	40.97	—	—
0.1409	41.35	—	—
0.1708	41.70	42.53	43.42
0.1943	41.99	42.90	—
0.2219	42.33	43.26	44.34
0.2487	42.70	—	
0.2782	43.16	—	
0.3006	43.50	—	
0.3130	43.70	—	
0.3311	43.99	—	
0.3513	44.30	—	
0.3670	44.58	45.79	
0.3820	44.90		
0.3962	45.12		
0.4120	45.43		
0.4304	45.75		

the aqueous solution, its mole fraction being 0.0115, at 1 atm and 10°C because the bubbling pressure at this concentration is about 12 kg/cm^2, so that the extrapolation has been done on the volume from 20 and 30 kg/cm^2 to 1 atm. Aqueous solution of the mole fraction of acetylene N_2=0.0159 turns to the solid gas hydrate at 10°C and acetylene gas bubbles at 25 and 40°C so that the measurements of the volume can not be done at these temperatures. As shown in Table 1, the temperature dependence of the specific volume of pure water at 30 kg/cm^2 is in accordance with that at 1 atm, and the compressibility in Table 1 is larger by about 15% than the result previously published[9]. However, the influence on the partial molal volume due to this error contained in the values of the compressibility is quite negligible.

Acetylene-benzene, acetylene-acetone, acetylene-methanol systems The experimental results at 30 kg/cm^2 for these systems are shown in Tables 2, 3 and 4 in the term of the mean molal volume and in Fig. 3 the mean molal volume of these solutions at 30 kg/cm^2 are plotted against the mole fraction of acetylene. The partial molal volumes are calculated according to the Bakhuis-Rooseboom method from Fig. 3 and their results are tabulated in Tables 5, 6 and 7. The partial molal volume depends upon the concentration. In Fig. 4 the difference of the partial molal volume

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[9] E. H. Amagat, *Ann. Chim. Phys.*, (6) **29**, 68, 505 (1893)
R. Kiyama, H. Teranishi and K. Inoue, *This Journal*, **23**, 20 (1953)

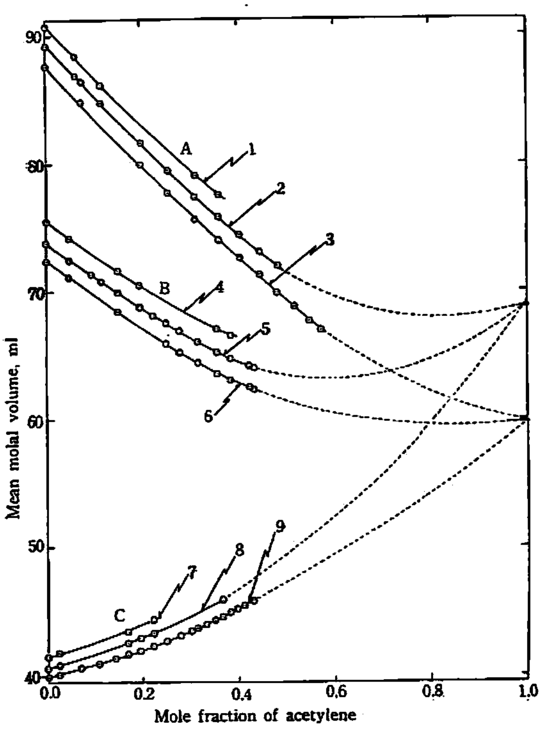

Fig. 3 Mean molal volume plotted against mole fraction of acetylene at 30 kg/cm²

A
acetylene+benzene
curve 1: 40°C
2: 25°C
3: 10°C

B
acetylene+acetone
curve 4: 40°C
5: 25°C
6: 10°C

C
acetylene+methanol
curve 7: 40°C
8: 25°C
9: 10°C

Table 5 Partial molal volumes of acetylene $\overline{V}_2$ (ml) and benzene $\overline{V}_1$ (ml) in acetylene-benzene solution at 30 kg/cm²

Mole fraction of acetylene	10°C		25°C		40°C	
	$\overline{V}_1$	$\overline{V}_2$	$\overline{V}_1$	$\overline{V}_2$	$\overline{V}_1$	$\overline{V}_2$
0.0	87.61	48.2	89.19	50.6	90.72	52.6
0.1	87.6	48.2	89.2	50.6	90.7	52.6
0.2	87.4	49.2	89.0	51.2	—	—
0.3	87.0	50.6	88.4	53.2	89.4	56.4
0.4	85.4	53.5	87.0	55.6		
0.5	84.0	55.2	85.5	57.5		
0.6	82.3	56.6				
dilute conc. 9)		48.7		50.3		52·0

of acetylene in the solutions and the molal volume of liquid acetylene is plotted against the mole fraction of acetylene at 10°C and 30 kg/cm², where the molal volume of liquid acetylene in equilibrium with its vapor at 10°C (its vapor pressure =33.9 atm), that is, 59.9 ml 10) is taken as the molal volume of liquid acetylene at 10°C and 30 kg cm². As seen from Fig. 4 and Tables 5, 6 and 7, the partial molal

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10) *Int. Crit. Tables*, 3, 230

Table 6 Partial molal volumes of acetylene $\bar{V}_2$ (ml) and acetone $\bar{V}_1$ (ml) in acetylene-acetone solution at 30 kg/cm^2

Mole fraction of acetylene	10°C		25°C		40°C	
	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1$	$\bar{V}_2$
0.0	72.30	45.8	73.75	47.8	75.40	49.2
0.1	72.3	45.8	73.7	48.1	75.4	49.6
0.2	71.9	47.3	73.6	49.0	75.1	51.0
0.3	71.1	49.6	72.6	51.7	74.0	54.5
0.4	69.2	53.1	71.0	54.6	72.5	57.0
0.5	67.6	55.2				
dilute conc. [5]		46.7		48.0		50.2

Table Partial molal volumes of acetylene $\bar{V}_2$ (ml) and methanol $\bar{V}_1$ (ml) in acetylene-methanol solution at 30 kg/cm^2

Mole fraction of acetylene	10°C		25°C		40°C	
	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1$	$\bar{V}_2$
0.0	39.98	47.5	40.59	49.3	41.43	51.5
0.1	39.9	49.7	40.4	52.2	41.2	53.2
0.2	39.4	53.0	40.1	52.7	40.6	57.2
0.3	38.7	55.0	39.3	55.5		
0.4	38.3	56.3				

Table 8 Compressibilities of acetylene-acetone solution and solvents, $\beta \times 10^5$

Mole fraction of acetylene	Acetone soln.			Benzene			Methanol		
	10°C	25°C	40°C	10°C	25°C	40°C	10°C	25°C	40°C
0.000	8.9	13	16	8.0	9.8	12	6.5	10	14
0.054		13							
0.094		12							
0.168		11							

volume of acetylene in methanol solution increases with the mole fraction of acetylene even from very dilute concentration, but in the other solutions there is a range up to about 0.15 mole fraction of acetylene in which the partial molal volume of acetylene is constant, that is to say, Ångstrom's rule[11] is held. The results of the present investigation at dilute concentration are fairly in accordance with Horiuti's results[5] at 1 atm in benzene and acetone solution as shown in the Tables.

The compressibility of the pure solvents and that of acetone solution at 25°C are given in Table 8. The compressiblity of the pure solvents given in Table 8 is

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[11] K. Ångstrom, *Wied Ann.*, **15**, 297 (1882), **33**, 223 (1888)

Table 9 Comparison of solubility of acetylene in methanol obtained in the present investigation with the results previously published at 10°C

Bubbling pressure, kg/cm^2	Mole fraction of acetylene	
	present	previous[1]
5.5	0.1068	0.113
10.6	0.1943	0.202
17.4	0.3006	0.316
21.5	0.3670	0.393

the average values between 1 atm and 30 kg/cm^2 and that of the acetone solution is the average between 10 and 30 kg/cm^2. The dependence of the compressibility upon the concentration is very small on account of the limited concentration range in the present investigation.

In Table 9, the solubility obtained from the pressure at which acetylene dissolved in methanol begins to bubble at 10°C is compared with the results of the previous report on the solubility of acetylene in methanol. The deviation of the present result from the previous one, which is about several per cent, is elucidated from the defects of both methods, because the solubility from the bubbling pressure is apt to be smaller on account of the difficulty of dissolution of the gas contaminated in acetylene and the previous apparatus for solubility measurement is apt to give a larger value on account of the large difference of pressure between the outside and inside of the sampling valve.

Considerations

Hildebrand *et al.*[12] reported that the partial molal volumes in nonpolar liquids increase strongly with decreasing internal pressures of the solvents. The results of the present investigation are in accordance with their observation, except in methanol solution, although the polar solvents are involved. And the exceptional decrease of the partial molal volume of acetylene in aqueous solution is explained by the larger internal pressure of water than those of any other solvents. Masterton[13] attributed the cause of the marked decrease of the partial molal volume of methane, ethane and propane in aqueous solutions to the largest internal pressure of water and also found that the partial molal volume of these lower hydrocarbons did not change linearly with temperature, that is, increased with the increase of temperature, but with smaller increase rate at higher temperatures. This behavior is different from that of benzene in aqueous solution which linearly increases with the increase of temperature. Masterton considers this difference of the behavior as one

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12) J. C. Gjaldbaek and J. H. Hildebrand, *J. Am. Chem. Soc.*, **72**, 1077 (1950)

13) W. L. Masterton, *J. Chem. Phys.*, **22**, 1830 (1954)

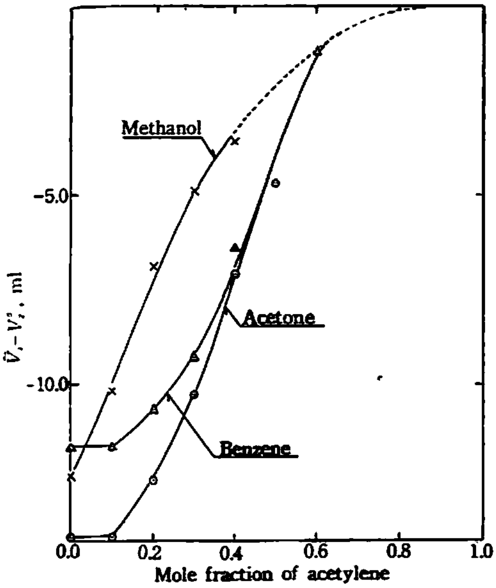

Fig. 4 Differences between partial molal volume and molal volume of acetylene in liquid state plotted against mole fraction of acetylene at 10°C and 30 kg/cm^2

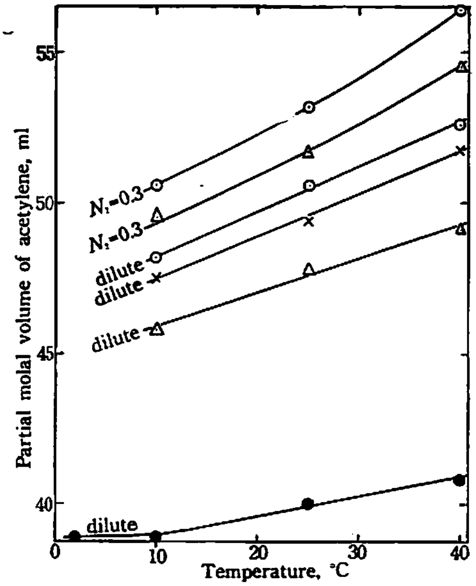

Fig. 5 Temperature dependence of partial molal volume of acetylene at 30 kg/cm^2

⊙ benzene △ acetone
× methanol ● water

of the indication that lower hydrocarbon molecules in aqueous solution are surrounded by orientated cages of water molecules. Aqueous solution of acetylene turns to the solid gas hydrate at temperatures lower than 16°C, if the concentration of acetylene is sufficiently high. Fig. 5 shows the temperature dependence of the partial molal volume of acetylene at 30 kg/cm^2. As seen from Fig. 5, the partial molal volume of acetylene in aqueous solution scarcely changes at temperatures lower than 10°C, but it increases almost linearly at higher temperatures and the rate of its increase with temperature is slower than those in other solutions. The results of the authors' measurements differ at the point of the temperature dependence of the partial molal volume from Masterton's results and the result of the present investigation seems to be more plausible than Masterton's result, because the thermal expansion coefficient in the crystalline state is generally smaller than in liquid state, although the solutes in these two investigations are different from each other. In the other solutions than aqueous solution the partial molal volume of acetylene changes almost linearly with temperature at dilute concentration, but it deviates from this linearlity at high concentration.

The change of volume on mixing, ΔV^M, may be given approximately by Eq. (1)[14],

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[14] *cf.* 3) p. 137

Table 10 Comparison of volume change on mixing observed with that calculated for acetylene-benzene solution at 10°C

Thermodynamic quantities	Mole fraction of acetylene	
	0.2	0.4
$\Delta\bar{H}_1$(cal/mole)	0.00	−1.20
$\Delta\bar{H}_2$(cal/mole)	2.24×10^2	3.80×10^2
ΔH^M(cc atm/mole)	1.85×10^3	3.34×10^3
ΔE^M(cc atm/mole)	1.83×10^3	3.28×10^3
$\frac{\partial(\Delta V^M)}{\partial t}$(cc/deg. mole)	−0.020	−0.025
$(\Delta V)^M_{\text{calcd.}}$ (cc/mole)	−5.5	−6.7
$(\Delta V)^M_{\text{obsd.}}$ (cc/mole)	−2.5	−3.9

$$\Delta V^M = \left(\frac{\partial \Delta E_V{}^M}{\partial P}\right)_{T,\,P=P_0} - T\left(\frac{\partial \Delta S_V{}^M}{\partial P}\right)_{T,\,P=P_0}, \tag{1}$$

where $\Delta E_V{}^M$ refers to the energy change on mixing at constant volume, $\Delta S_V{}^M$ the entropy change on mixing at constant volume. To the extent that the entropy on mixing is a function of random configuration and is assumed independent of heat interaction, the second term on the right hand side of Eq. (1) may be neglected and the Scatchard equation (2) is derived with some approximations,

$$\Delta V^M = \beta_0 \Delta E_V{}^M \tag{2}$$

where β_0 refers to the average compressibility of the isolated components. In Fig. 3, the straight lines joining the point at $N_2=0$ with the point at $N_2=1$ of the mean molal volume of each solution at each temperature corresponds to the ideal solution with no volume change on mixing the solvents and liquid acetylene and the deviation from this straight line indicates the volume change on mixing. In this case the molal volume of liquid acetylene is assumed to be equal to the molal volume of liquid acetylene in equilibrium with its vapor as stated above. As seen from Fig. 3, the negative volume change on mixing is observed for every acetylene solution. As stated qualitatively in the previous papers, the heat of solution of liquid acetylene may be negative in every solution discussed in this investigation, except benzene solution, so that the volume change on mixing is in accordance with Eq. (2) so far as the sign is concerned, because the energy change on mixing is surely approximated with the heat content change on mixing for these condensed systems as illustrated in Table 10 for benzene-acetylene solutions.

However, $\Delta E_V{}^M$ for benzene solution of acetylene is positive and the negative volume change on mixing observed in this investigation is incompatible with Eq. (2). This inconsistency may be attributed to the negligence of the second term on the right hand side of Eq. (1), which is related with the difference of the thermal expansion coefficient of the solution and the average one of the pure components by Eq. (3),

$$T\left(\frac{\partial \Delta S_T^M}{\partial P}\right)_T = -T\left(\frac{\partial \Delta V^M}{\partial T}\right)_P. \tag{3}$$

The results of the present investigation show that the thermal expansion coefficient of the solution is far less than the average one of the pure components and from this cause the large decrease of the volume seems to occur on mixing the solvents and liquid acetylene. The thermal expansion coefficient of liquid acetylene is calculated from the density of liquid acetylene in equilibrium with its vapor at each temperature. In Table 10 the results of the calculation according to Eq. (1) are given, with each term contributing to the volume change on mixing. $\Delta\overline{H}_2$ is calculated from the solubility of acetylene previously reported with necessary correction using the values of the partial molal volumes given in the present report, and the heat of dilution of the solvent $\Delta\overline{H}_1$ is calculated from the dependence of $\Delta\overline{H}_2$ upon the concentration. The result of the calculation of the volume change on mixing $(\Delta V)^M{}_{\text{calc.}}$ according to Eq. (1) is fairly in good accordance with the observed values $(\Delta V)^M{}_{\text{obs.}}$ and the difference between these two values seems to come from the uncertainty of the thermal expansion coefficient and the compressibility of liquid acetylene. For other solutions than benzene solution, the energy change on mixing at the mole fraction of acetylene $N_2=0.4$ is about -500 cal/mole at most and so the volume change calculated from Eq. (2) is about -1.5 ml/mole but the observed value is about -4.6 ml/mole in acetone solution and about -3.0 ml/mole in methanol solution, so that the second term of Eq. (1) will be important for these solutions.

From the above considerations, it is concluded that the second term on the right hand side of Eq. (1) dominates in such solutions as acetylene solutions and the entropy of mixing is never the function of random configuration and the large specific interaction between acetylene and the solvent is the characteristic of the acetylene solutions.

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