Solubility and Diffusivity of Carbon Monoxide in Liquid Methanol

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The solubility of carbon monoxide in liquid methanol was measured by the decrease in pressure due to absorption at pressures up to 1500 kPa and temperatures up to 140 °C. The mole fraction solubility was between 4.2×10^{-4} and 11×10^{-3}, and the Henry's law constants were about 250 MPa at temperatures lower than 80 °C and pressures up to 1000 kPa. The diffusivity of CO gas in methanol was determined by measuring the diameter and solution time of a single CO bubble in methanol over the temperature range from 25 °C to 90 °C at a pressure of 500 kPa. The diffusion coefficients ranged between 5×10^{-9} $m^2 \cdot s^{-1}$ and 9.5×10^{-9} $m^2 \cdot s^{-1}$ for the temperature range from 25 °C to 90 °C and increased as temperature increased. Empirical correlations for the solubility and diffusivity at various temperatures were given.

Introduction

The liquid phase methanol synthesis process, which starts with the carbonylation of methanol to methyl formate, followed by the hydrogenolysis of the formate, was studied to recover wasted or unused discharged heat from industrial sources for the thermal energy demands of residential and commercial areas by chemical reactions, such as methanol decomposition and synthesis reactions (Takemura et al., 1994).

$$CH_3OH + CO = CH_3OOCH \qquad +38.1\ kJ \cdot mol^{-1} \qquad (1)$$

$$CH_3OOCH + 2H_2 = 2CH_3OH \qquad +62.8\ kJ \cdot mol^{-1} \qquad (2)$$

A knowledge of the solubility and diffusion coefficient of CO gas in liquid methanol is important to evaluate the effect of the transport process in the reaction process because the reaction may be controlled by the transport process. The solubility of carbon monoxide in methanol was reported by Gjaldbaek (1948) at temperatures from 20 °C to 50 °C and at a pressure of 101 kPa. Tonner et al. (1983) gave the solubility of carbon monoxide in methanol at pressures up to 4000 kPa and temperatures of 25 °C and 50 °C by using a chromatographic technique to analyze equilibrated gas-in-liquid mixtures. Luhring and Schumpe (1989) determined the solubility of carbon monoxide in methanol at 20 °C and 101 kPa by measuring the pressure decrease due to absorption. This barometric method was also used to measure gas−liquid mass transfer coefficients in a mechanically agitated vessel, as reported by Albal et al. (1983). However, these data were limited to measurements at a narrow range of temperature and generally limited to atmospheric pressure. Reactions 1 and 2 occur at temperatures from 60 °C to 140 °C and pressures from 2000 kPa to 6000 kPa. It is necessary to measure the solubility over a wide range of pressure and temperature conditions.

Diffusion coefficients of gases in liquids have been measured mostly for low temperatures at atmospheric pressure, but rarely at high temperatures and pressures because of difficulties in measurement under such conditions. The measurement should be rapid due to difficulties in controlling temperature and pressure. An ideal method for this was suggested by Houghton et al. (1962) in which they estimated the diffusion coefficient by measuring the absorption rate of a single bubble attached to a wall. They derived a linear relationship between the absorption rate and diffusion coefficient by neglecting a transient term of Epstein and Plesset's (1950) equation of absorption rate for a bubble in an infinite liquid and considering the effect of the wall on the absorption rate (Liebermann, 1957). The advantages of this method are the measurement time is short by using a small bubble, the precision is well maintained by using an optical microscope, and the temperature can be easily controlled by using a small test cell in a temperature bath. Wise and Houghton (1966) used this method to measure the diffusivities of ten slightly soluble gases in water from 10 °C to 60 °C and obtained good agreement with results by other methods. However, in the case of relatively high solubility, the transient term of Epstein and Plesset's (1950) equation becomes sufficiently large and cannot be neglected. Moreover, natural convection may be generated by a concentration difference between the pure liquid and the gas-absorbed liquid surrounding the bubble. Therefore, the diffusivity measurement should be carried out in regions where the natural convection is negligible.

Recently, Takemura et al. (1996) studied both experimentally and theoretically the absorption process of a single gas bubble into a liquid. The effect of natural convection due to the concentration difference was estimated numerically by solving the gas diffusion equation in the liquid and the vorticity transport and Poisson equations for the stream function. They estimated experimentally the diffusion coefficient of gas in liquid by measuring the solution time of a single gas bubble under a plate. Both the experimental and numerical results reveal that when the initial bubble diameter is small enough, the effect of the density-induced natural convection is negligible. In this paper, measurements of diffusion coefficient for carbon monoxide in liquid methanol over a wide temperature range are presented by measuring the solution time and the diameter of single small bubbles.

Solubility

Experimental Apparatus and Method. The experiments were conducted in a stainless steel vessel which is 102 mm in diameter, 600 mm in height, and 4.9 dm^3 in volume. The gas solubilities were determined by a barometric method (Luhring and Schumpe, 1989) which involves the measurement of the volumes of the gas and liquid, the temperature, and the total pressure change due

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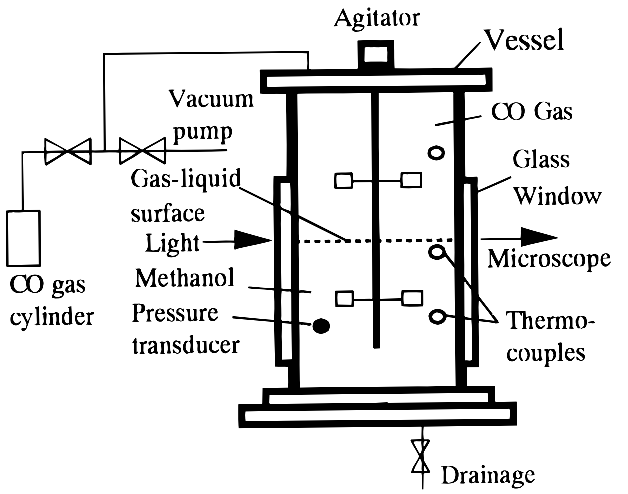

Figure 1. Schematic diagram of experimental apparatus for solubility measurement.

Table 1. Mole Fraction Solubility and Henry's Law Constant at 30 °C at Various Pressures

P_2/kPa	10^4x	H/MPa
73.5	3.13	234.6
145.9	6.03	242.1
338.3	13.17	256.8
402.1	15.50	259.5
465.3	17.86	260.5
631.2	23.97	263.3
868.5	32.87	264.2
1053.5	39.13	269.2
1256.4	46.67	269.2

to gas absorption. Figure 1 shows the schematic diagram of the experimental apparatus. Glass windows were installed for the observation and the measurement of the liquid level by a microscope. The pressure was measured by a semiconductor pressure transducer and could be read to ±0.1 kPa. The temperature was measured by chromel-alumel thermocouples with a precision of ±1 deg. The temperature of the liquid was increased by electric heaters installed on the vessel. The liquid temperature was controlled within ±1 deg by a PID (proportion-integration-differentiation) controller. A cooling coil in the test vessel was used to lower the temperature when necessary. The methanol was purchased from Wako Pure Chemical Industries Ltd. with a purity of 99.8%. The CO was from Takachiho Chemical Industries Ltd. with a purity of 99.95%.

Experiments were carried out using the following procedures: (a) the required amount of liquid methanol was placed in the vessel; (b) the liquid was degassed by using a vacuum pump and a magnetic agitator; (c) when the temperature reached the desired value, the agitator was stopped and the CO gas was added slowly to reach a desired pressure; (d) when the temperatures of liquid and gas phases were equal, thermal equilibrium was reached; (e) the initial pressure, temperature, and level of liquid were recorded; (f) agitation was started; (g) after about 10 min, the agitation was stopped; the pressure did not change at the saturation state for a definite temperature; (h) the pressure and temperature were recorded, and the amount of dissolved gas was derived.

The moles of dissolved gas were calculated by

$$n_2 = \Delta P_2 V_2/(RT) \quad (3)$$

where P_2 is the partial pressure of CO gas which was obtained by subtracting the methanol vapor pressure from the total pressure, V_2 is the volume of gas, R is the gas constant (8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$), and T is the absolute temperature. The moles of methanol are

$$n_1 = \rho_1 V_1/M_1 \quad (4)$$

where ρ_1, V_1, and M_1 are the density, the volume, and the molecular weight (32) of liquid methanol, respectively.

The mole fraction of dissolved gas (n_2) in methanol (n_1) is

$$x = n_2/(n_1 + n_2) \quad (5)$$

Then, Henry's law constant is

$$H = P_2/x \quad (6)$$

The measurement errors for pressure, volume, and temperature were 0.2%, 0.2%, and 0.75%, respectively. Then, the measurement errors for n_2, x, and H were estimated to be about 1.5%. The reproducibility of solubility was within ±5% for triplicate measurements at 1000 kPa and various temperatures.

Experimental Data and Discussion. Table 1 shows the mole fraction solubility and Henry's law constant of carbon monoxide in methanol at 30 °C and partial pressures from 73.5 kPa to 1256.4 kPa. All the partial pressures are values at saturation. The ranges of partial pressure decrease due to absorption are from 20 kPa at 73.5 kPa to 300 kPa at 1256.4 kPa. The mole fraction solubility increases from 3.13×10^{-4} to 46.67×10^{-4} as the pressure increases from 73.5 kPa to 1256.4 kPa. The averaged value of Henry's law constant is around 250 MPa. The Henry's law constant shows about a 15% increase as the pressure increases from 73.5 kPa to 1256.4 kPa. The extrapolation value at 30 °C and 101 kPa from Table 1 is 4.24×10^{-4}, which is 13% higher than Gjaldbaek's data (1948) of 3.76×10^{-4}. As a comparison, the mole fraction solubility of carbon monoxide in liquid water is about 2×10^{-5} at 30 °C and 101 kPa (Hodgman, 1963). This is about 20 times less than that in methanol. Carbon monoxide is more soluble in methanol than in water.

Table 2 shows the mole fraction solubility at temperatures from about 30 °C to 140 °C. The data are arranged as group 1 (503.8 kPa to 602.3 kPa), group 2 (896.3 kPa to 1111.4 kPa), and group 3 (1331 kPa to 1749.3 kPa) according to the ranges of partial pressures of carbon monoxide. The mole fraction solubility of carbon monoxide is between 1.93×10^{-3} to 10.7×10^{-3}.

Figure 2 shows Henry's law constant H calculated from the data tabulated in Table 2. The values of H are almost constant at pressures less than about 1100 kPa. Though the data of groups 1 and 2 show maximum values at about 60 °C, the Henry's law constants are about 250 MPa with a variation of ±4% for temperatures less than 80 °C and decrease when the temperatures are higher than 80 °C. At pressures higher than 1100 kPa, the Henry's law constant is about 10% higher than that at pressures less than 1000 kPa. The lines in Figure 2 are the calculated values using the following empirical correlation based on the authors' experimental data. The correlation expresses the experimental data within ±12%. Extrapolation to a wider range of pressure should be done on further experimental data.

$$\ln(H/\mathrm{MPa}) = 203.6 - 9475.8/(T/\mathrm{K}) - 29.2\ln(T/\mathrm{K}) + 1.65 \times 10^{-7}(P/\mathrm{Pa}) \quad (7)$$

The open circles in Figure 2 show Gjaldbaek's data (1948) at temperatures of (20, 35, and 50) °C and 101 kPa. They

Table 2. Mole Fraction Solubility of CO in Methanol

group 1 P_2 = (503.8−602.3) kPa			group 2 P_2 = (896.3−1131) kPa			group 3 P_2 = (1331−1749.3) kPa		
t/°C	P_2/kPa	10^3x	t/°C	P_2/kPa	10^3x	t/°C	P_2/kPa	10^3x
27.3	503.8	1.93	30.4	896.3	3.54	30.8	1331.0	4.88
42.7	528.8	2.07	40.2	923.7	3.63	41.9	1388.2	4.91
49.5	534.8	2.10	50.3	965.5	3.79	49.8	1440.4	5.01
61.1	562.6	2.22	60.9	1000.2	3.91	59.6	1489.7	5.16
69.3	576.3	2.30	70.6	1024.3	4.13	71.0	1540.0	5.51
80.4	594.8	2.45	80.7	1049.9	4.36	80.1	1592.9	5.57
89.2	602.3	2.64	92.5	1091.3	4.47	91.8	1645.7	5.88
99.9	584.6	3.18	101.5	1111.4	4.80	100.4	1669.3	6.39
			111.2	1131.0	5.10	120.4	1749.3	7.22
			120.8	1101.7	6.10	137.6	1591.8	10.70
			129.8	1130.0	6.36			
			140.4	1078.6	7.56			

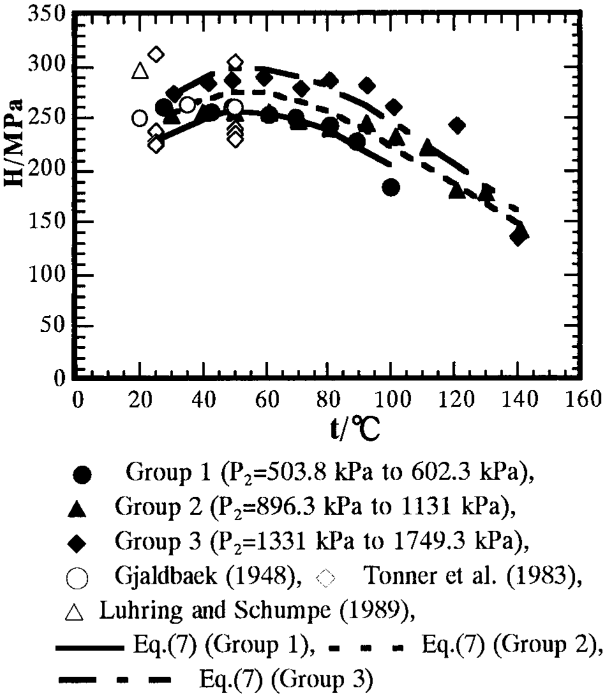

Figure 2. Henry's law constants at various temperatures and pressures.

are in agreement with our results at pressures less than 1100 kPa within 5%. Luhring and Schumpe's data (1989) at 20 °C and Tonner et al.'s data (1983) at 25 °C and 50 °C are also shown in the same figure. The former is 15% higher than the author' values, and the average of the latter is in agreement with authors' results at pressures less than 1100 kPa within 2%.

Diffusion Coefficient

Estimation Method. As mentioned in the Introduction, Takemura et al. (1996) obtained theoretically the results of the absorption process of a single gas bubble into a liquid by numerically solving the gas diffusion equation in the liquid. The diffusion coefficients at various temperatures were estimated by measuring the diameter and solution time of a small single CO bubble in methanol and comparing the experimental data with the theoretical results (numerical solutions). Small bubbles of diameter less than 250 μm were used to minimize the effect of density-induced natural convection on the absorption process (Takemura et al., 1996). The difference between our method and Houghton et al.'s (1962) method is that we use a rigorous numerical solution (Takemura et al., 1996) for the single bubble solution in a liquid instead of an approximate analytical solutions used by Houghton et al. (1962) and Wise and Houghton (1966).

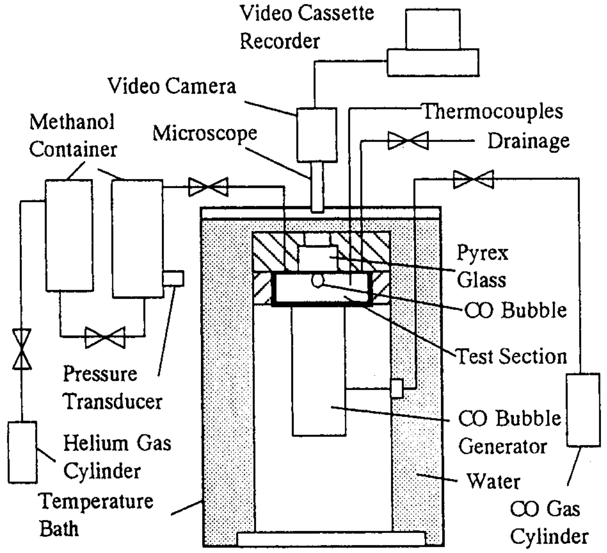

Figure 3. Schematic diagram of experimental apparatus of single bubble solution.

Table 3. Numerical Solution Time

b	1.0	2.0	3.0	4.0	5.0
t^*	0.753	0.870	0.936	0.981	1.014
b	6.0	7.0	8.0	9.0	10.0
t^*	1.041	1.062	1.080	1.096	1.109

Theoretical Results of Solution Time. Table 3 shows the nondimensional solution time t^* with parameter b for the absorption process of a single CO bubble in methanol (Takemura et al., 1996). The nondimensional time t^* is expressed as $t^* = 2D\rho_1 c_w t_s/(\rho_2 R_0^2)$. The parameter b is the density ratio of the gas inside the bubble to the saturated gas in liquid, $b = \rho_2/(\rho_1 c_w) = HM_1/(\rho_1 RTM_2)$, where D is the diffusion coefficient, c_w is the saturation concentration of CO gas in liquid, t_s is the solution time, ρ_2 is the density of CO gas, R_0 is the initial bubble radius, and M_2 is the molecular weight of CO gas. As an example, the values of parameter b and t^* are 3.798 and 0.972 at 60 °C and 500 kPa. Details of the theoretical solution were given elsewhere by Takemura et al. (1996).

Experimental Apparatus and Results of Single CO Bubble Solution in Methanol. Figure 3 shows the apparatus for measuring the solution time and diameter of a single CO bubble. The apparatus consisted of a test section, a bubble generator, a temperature bath, a methanol container, a carbon monoxide cylinder, an optical microscope, a CCD camera, and a video cassette recorder. The test section was 5 mm in diameter and 3 mm in height.

Table 4. Initial Diameter of Bubble and Solution Time

t = 25.7 °C		t = 60 °C		t = 80 °C	
D_0/μm	t_s/s	D_0/μm	t_s/s	D_0/μm	t_s/s
113	1.35	124	0.97	165	1.30
125	1.66	194	2.73	206	1.73
138	1.89	206	2.80	253	2.90
206	4.12	259	3.37		

Table 5. Diffusion Coefficients of Carbon Monoxide in Methanol

t/°C	25.7	30	40	50	60	70	80	90
$10^9D/\mathrm{m^2 \cdot s^{-1}}$	5.0	5.9	6.3	7.5	7.8	8.5	9.0	9.5

The bubble was kept steady under a plate of Pyrex glass. The temperature was measured by thermocouples inserted in the test section. The bubble generator was under the test section, and the bubble was generated by regulating the pressure difference between the generator and test section within several kilopascal. The test section was installed in a temperature bath to keep the temperatures of the test section in uniform distribution. The liquid in the test section was changed to fresh liquid from a methanol container after each experiment. The diameter of the bubble became smaller as the solution and diffusion process started. The bubbles were photographed using the CCD camera through the optical microscope and recorded using the video cassette recorder at 30 frames per second. The diameter of the bubble and solution time were measured for every frame. Table 4 shows typical experimental data of the initial diameter D_0 and solution time t_s for liquid temperatures of 25.7 °C, 60 °C, and 80 °C at 500 kPa. The measurement error of the initial diameter is 1.5%.

Results of Diffusion Coefficient. At least three single bubbles with initial diameters less than about 250 μm were used to obtain the diffusion coefficient at every temperature. The average value of the diffusion coefficients at 25.7 °C is $5 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$. Table 5 shows the results of diffusion coefficients at temperatures from 25.7 °C to 90 °C. The diffusion coefficients are in the range of $5 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$ to $9.5 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$ and increase with temperature. The average error is estimated to be ±5%. The following empirical correlation for the diffusion coefficient was obtained on the basis of the experimental data.

$$D/\mathrm{m^2 \cdot s^{-1}} = 167.1 \times 10^{-9} \exp[-1027.6/(T/\mathrm{K})] \qquad (8)$$

The correlation expresses the diffusion results within ±8%.

Conclusions

The solubility and diffusion coefficient of carbon monoxide in liquid methanol were measured at various pressures and temperatures. The mole fraction solubilities are between 4.2×10^{-4} and 10.7×10^{-3} for pressures from atmospheric pressure up to 1500 kPa, and for temperatures from 30 °C to 140 °C. The Henry's law constants are about 250 MPa for temperatures less than 80 °C and pressures up to 1000 kPa. The diffusion coefficients are between $5 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$ and $9.5 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$ for the temperature range from 25 °C to 90 °C, and they increase as temperature increases.

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