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Solubility of Hydrogen in Liquid Methanol and Methyl Formate at 20 °C to 140 °C

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The solubilities of hydrogen gas in liquid phase methanol and methyl formate were measured under pressures up to 1500 kPa and temperatures to 140 °C. The mole fraction solubilities were between 7.9 $\times 10^{-4}$ and 6.3 $\times 10^{-3}$ for H_2 in methanol and between 7 $\times 10^{-4}$ and 6.9 $\times 10^{-3}$ for H_2 in methyl formate. The Henry's law constants were about 620 MPa for H_2 in methanol and 630 MPa for H_2 in methyl formate at a temperature of 20 °C. The Henry's law constants show a decrease with increase of temperature. Empirical correlations for solubilities at various temperatures were given on the basis of the experimental data.

Introduction

The two-stage liquid phase methanol synthesis process which starts with carbonylation of methanol to methyl formate, then followed by 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 (Takemura et al., 1994).

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

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

A knowledge of the solubilities of CO gas and H_2 gas in liquid methanol and methyl formate 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 authors (Liu et al., 1996) reported the solubility of CO gas in liquid methanol at pressures up to 1500 kPa and temperatures up to 140 °C. Choudhary et al. (1986) gave the solubility of hydrogen in methanol at temperatures of (20 to 55) °C and pressures of (439 to 2145) kPa. Wainwright et al. (1987) reported the solubility of H_2 in methanol and methyl formate at a temperature of 18 °C and pressures up to 5 MPa by using both a chromatographic technique to analyze equilibrated gas-in-liquid mixtures and a barometric method (Albal et al., 1983; Luhring and Schempe, 1989). However, their data were restricted to temperatures less than 55 °C. Catalytic reactions 1 and 2 occur at temperatures from 60 °C to 140 °C and pressures from 2000 kPa to 6000 kPa (Liu et al., 1988). The purpose of this study is to obtain the experimental data of solubilities of H_2 gas in liquid methanol and methyl formate at a wide range of pressure and temperature conditions. The experimental solubility data were measured without using catalyst.

Experimental Apparatus and Method

The experimental apparatus and method were the same as reported by Liu et al. (1996). The experiments were conducted in a magnetically agitated 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 to gas absorption. The pressure was measured by a semiconductor pressure transducer and could be read to 0.1 kPa. The temperature was measured by thermocouples with a precision of ±1 °C. The methanol and methyl formate were purchased from Wako Pure Chemical Industries Ltd. with purities of 99.8% and 97.5%. The hydrogen gas was from Takachiho Chemical Industries Ltd. with a purity of 99.999%. For the case of solution of hydrogen in methanol, the moles of dissolved gas were calculated by

$$n_{H_2} = \Delta P_{H_2} V_g/(RT) \qquad (3)$$

where P_{H_2} is the partial pressure of H_2 gas which was obtained by subtracting the liquid vapor pressure from the total pressure, V_g is the volume of the gas, R is the gas constant (R = 8.314 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$), and T is the absolute temperature. The mole fraction of dissolved gas in methanol is

$$x_{H_2} = n_{H_2}/(n_{MeOH} + n_{H_2}) \qquad (4)$$

Then, Henry's law constant is

$$H_{H_2} = P_{H_2}/x_{H_2} \qquad (5)$$

where n_{MeOH} is the moles of methanol. The measurement errors for n, x, and H were estimated to be about 1.5% (Liu et al., 1996). The reproducibility of solubility was within ±5%.

Experimental Results and Discussion

Table 1 gives the mole fraction solubility for hydrogen in methanol. The data are arranged as (505.9 to 595.7) kPa, (914.8 to 1190.7) kPa, and (1337.3 to 1658.5) kPa according to the ranges of partial pressures of hydrogen. The temperatures ranged from 23.1 °C to 140.3 °C. The mole fraction solubilities of hydrogen are between 0.79 $\times 10^{-3}$ and 6.34 $\times 10^{-3}$ and increase as the temperature increases. Table 2 shows the mole fraction solubility for hydrogen in methyl formate. The mole fractions of hydrogen are between 0.71 $\times 10^{-3}$ and 6.87 $\times 10^{-3}$ and also

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Table 1. Mole Fraction Solubility of Hydrogen in Methanol

P_{H_2} = (505.9−595.7) kPa			P_{H_2} = (914.8−1190.7) kPa			P_{H_2} = (1337.3−1658.5) kPa		
t/°C	P_{H_2}/kPa	$10^3 x_{H_2}$	t/°C	P_{H_2}/kPa	$10^3 x_{H_2}$	t/°C	P_{H_2}/kPa	$10^3 x_{H_2}$
23.1	505.9	0.79	23.2	914.8	1.50	26.5	1337.3	2.12
30.5	516.6	0.92	30.8	936.2	1.59	29.0	1326.2	2.19
40.8	536.2	1.03	40.2	966.7	1.75	41.1	1406.8	2.49
50.1	549.7	1.13	49.7	995.5	1.93	50.3	1425.1	2.85
62.0	566.5	1.34	59.9	1024.0	2.15	60.5	1468.1	3.08
71.8	582.3	1.42	69.3	1056.3	2.35	70.3	1518.0	3.40
81.0	585.6	1.67	80.0	1088.5	2.62	79.9	1541.6	3.75
90.4	594.3	1.88	90.4	1135.9	2.74	90.3	1627.6	3.78
100.8	595.7	2.19	100.9	1141.5	3.27	100.9	1658.5	4.33
			109.8	1141.1	3.74			
			119.7	1190.7	3.76			
			129.1	1186.1	4.37			
			140.3	1071.2	6.34			

Table 2. Mole Fraction Solubility of Hydrogen in Methyl Formate

P_{H_2} = (479.3−541.9) kPa			P_{H_2} = (958.8−1175.0) kPa			P_{H_2} = (1375.7−1644.0) kPa		
t/°C	P_{H_2}/kPa	$10^3 x_{H_2}$	t/°C	P_{H_2}/kPa	$10^3 x_{H_2}$	t/°C	P_{H_2}/kPa	$10^3 x_{H_2}$
20.1	479.3	0.71	22.5	958.8	1.44	22.9	1375.7	2.50
30.9	492.8	0.92	31.6	984.7	1.85	30.6	1402.4	2.97
40.7	503.6	1.20	41.0	1013.4	2.22	40.7	1443.8	3.57
49.9	505.5	1.63	49.8	1025.1	2.80	50.0	1477.8	4.17
61.7	528.1	1.78	62.2	1066.3	3.27	59.6	1507.2	4.76
72.1	541.9	2.05	72.4	1099.9	3.70	69.6	1577.0	5.06
80.9	541.5	2.50	80.7	1094.5	4.57	80.8	1631.5	5.68
90.7	538.5	3.05	90.4	1156.4	4.38	90.7	1644.0	6.87
100.1	541.4	3.41	100.5	1175.0	5.11			

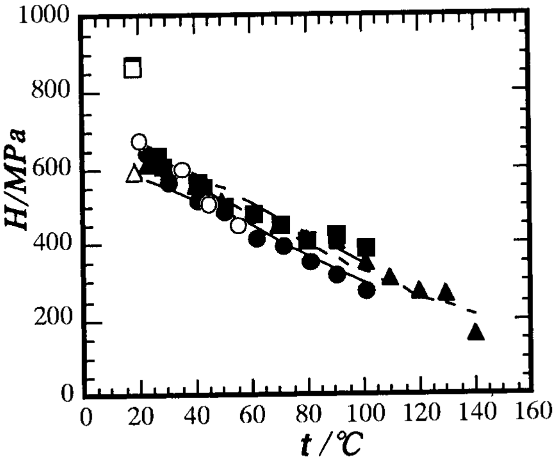

Figure 1. Henry's law constants of hydrogen in methanol at various pressures and temperatures: (●) (505.9−595.7) kPa; (▲) (914.8−1190.7) kPa; (■) (1337.3−1658.5) kPa; (○) Choudhary et al. (1986); (△) Wainwright et al. (1987) (gas chromatograph); (□) Wainwright et al. (1987) (barometric method); (—) eq 6 ((505.9−595.7) kPa); (- - -) eq 6 ((914.8−1190.7) kPa); (— —) eq 6 ((1337.3−1658.5) kPa).

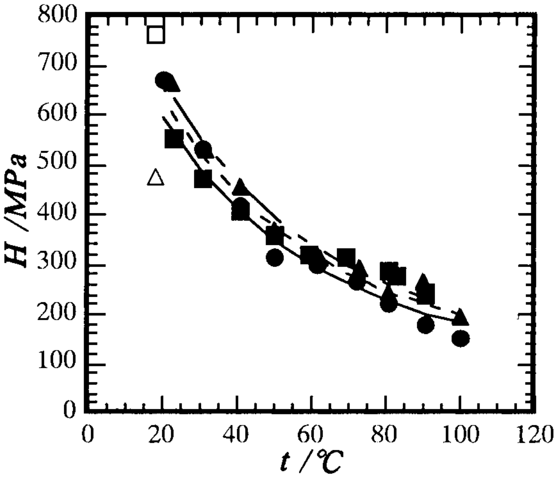

Figure 2. Henry's law constants of hydrogen in methyl formate at various pressures and temperatures: (●) (479.3−541.9) kPa; (▲) (958.8−1175.0) kPa; (■) (1375.7−1644.0) kPa; (△) Wainwright et al. (1987) (gas chromatograph); (□) Wainwright et al. (1987) (barometric method); (—) eq 7 ((479.3−541.9) kPa); (- - -) eq 7 ((958.8−1175.0) kPa); (— —) eq 7 ((1375.7−1644.0) kPa).

increase as the temperature increases. The mole fraction solubilities of H_2 in methanol are smaller than those for CO in methanol (Liu et al., 1996): they are 50% and 80% of those for CO in methanol at 30 °C and 140 °C under about 1000 kPa. The mole fraction solubilities of H_2 in methyl formate are almost the same as the values for H_2 in methanol near 20 °C but become higher as the temperature increases: they are increased about 56% at 100 °C for 550 kPa to 1100 kPa.

Figures 1 and 2 show Henry's law constants H at various temperatures for hydrogen in methanol and methyl formate, respectively. The Henry's law constants are calculated by eqs 3−5. As shown in these figures, the Henry's law constants decrease when the temperatures increase. The Henry's law constants vary about 10% for pressures up to 1500 kPa. The lines in Figures 1 and 2 are the calculated values using the following empirical correlations based on the authors' experimental data. The correlations express the experimental data within ±10%.

$$\ln(H/\mathrm{MPa}) = 122.3 - 4815.6/(T/\mathrm{K}) - 17.5\ln(T/\mathrm{K}) + 1.4\times10^{-7}(P/\mathrm{Pa}) \quad \text{for } H_2 \text{ in methanol} \quad (6)$$

$$\ln(H/\mathrm{MPa}) = -9.7 + 2232.2/(T/\mathrm{K}) + 1.5\ln(T/\mathrm{K}) + 1.3\times10^{-7}(P/\mathrm{Pa}) \quad \text{for } H_2 \text{ in methyl formate} \quad (7)$$

The open circle symbols in Figure 1 show the data of Choudhary et al. (1986) at (20 to 55) °C at pressures of (439 to 2145) kPa. They are in agreement with authors' experimental data within ±8%. The other open symbols in Figure 1 show the data of Wainwright et al. (1987) at 18 °C for the pressures up to 5 MPa. They obtained two groups of data by two measurement methods. The open triangle symbols show the data by using gas chromatography to analyze the solubility of hydrogen dissolved in methanol, and the open square symbols show the data by the barometric method which is the same as the authors. Their data obtained by the barometric method are higher than the authors' data, and their data of 600 MPa obtained by the gas chromatography method are 5% smaller than the authors'.

The open symbols in Figure 2 show the data of Wainwright et al. (1987) for hydrogen in methyl formate at 18 °C for the pressures up to 5 MPa. Their value of about 760 MPa obtained by the barometric method is 20% higher than the authors'.

Conclusions

The solubilities of hydrogen gas in liquid phase methanol and methyl formate were measured under pressures up to 1500 kPa and temperatures up to 140 °C. The solubilities ranged between 7.9×10^{-4} and 6.3×10^{-3} for H_2 in methanol and between 7×10^{-4} and 6.9×10^{-3} for H_2 in methyl formate. The Henry's law constants are about 620 MPa for H_2 in methanol and 630 MPa for H_2 in methyl formate at the temperature of 20 °C. The Henry's law constants show decreases with the increase of temperature.

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