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Solubility of Hydrogen in Alcohols and Esters

Mark S. Wainwright,* Thomas Ahn, and David L. Trimm

School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Kensington, New South Wales, 2033 Australia

Noel W. Cant

School of Chemistry, Macquarie University, North Ryde, New South Wales, 2113 Australia

The solubility of hydrogen in various alcohols and esters has been measured at pressures up to ca. 5 MPa by gas chromatographic analysis of equilibrated gas-in-liquid mixtures from a stirred autoclave vessel. Typical dilute solution behavior was observed, and the Henry's law coefficients for hydrogen solubility in normal alcohols and corresponding esters at 291 K are presented. A batch gas absorption technique based on pressure and volume measurements was shown to significantly underestimate solubility when values of hydrogen solubility in methyl alcohol and methyl formate were compared with those obtained by analysis of the gas dissolved in the liquid phase.

Introduction

There has recently been considerable interest in the liquid-phase synthesis of methanol (*1*). This process involves the carbonylation of the alcohol

$$\mathrm{ROH + CO \rightarrow HCOOR} \qquad (1)$$

to produce a formate ester, and a simultaneous or sequential hydrogenolysis step to produce the parent alcohol and a molecule of methanol. This hydrogenolysis, which is conducted as a slurry phase reaction at pressures up to 10 MPa (*1*, *2*), can be represented as

$$\mathrm{HCOOR + 2H_2 \rightarrow ROH + CH_3OH} \qquad (2)$$

Reactions conducted by using this form of contacting are frequently limited by mass-transfer considerations and it is therefore essential to have some knowledge of the solubility of the reacting gases in the liquid reactants and products. In a recent study (*3*) we presented CO solubility data for a wide range of alcohols. A review of the literature reveals that studies of H_2 solubility in lower alcohols have been made for methanol (*4*-*9*), ethanol (*4*, *9*), 1-propanol (*4*, *9*, *10*), and 1-butanol (5, 9-11). Measurements for corresponding esters have been limited to methyl acetate (*9*, *12*) and ethyl acetate (*9*, *13*, *14*). Many of those investigations were restricted to pressures less than 0.2 MPa. The present study was therefore undertaken to provide solubility data at pressures up to around 5 MPa on alcohols and esters that have been studied in hydrogenolysis reactions in this laboratory.

Experimental Section

The measurements were carried out in the apparatus used in the earlier study of CO solubility (*8*). It consisted of a 300-cm^3 stirred autoclave (Autoclave Engineers, PA) which was rated to 34 MPa. The experiments were conducted in a constant temperature room at 291 K. The temperature of the liquid in the autoclave was measured with a calibrated 1 mm o.d., stainless-steel sheathed, chromel-alumel thermocouple, the output of which was continuously monitored by using a digital voltmeter. The temperature of the liquid in the autoclave was 291 ± 1 K for all experiments. The pressure was measured to within ±10 kPa with a standardized Bourdon-type gauge. More complete details and a diagram of the apparatus are presented elsewhere (*3*).

Solubility measurements were carried out by initially placing 200 cm^3 of the solvent of interest in the autoclave and pressurizing the system to the desired level (1-5 MPa) from a cylinder of hydrogen. After stirring for 10 min to achieve equilibration, a sample of the liquid phase was taken for analysis by drawing a fine stream from the autoclave through a four-port Valco HPLC valve. The valve which had an internal loop volume of 1.0 μL was maintained at the same temperature as the autoclave (291 K). The flow was then shut off after the valve, and after about 30 s was allowed for pressure equilibration between the valve and the autoclave, the 1-μL sample was switched into a stream of high-purity nitrogen carrier gas (25 $cm^3\ min^{-1}$) where it vaporized and was carried to a Gow-Mac gas chromatograph fitted with a thermal conductivity detector. A 1.8-m column of Porapak N, maintained at 378 K, was used to separate the hydrogen peak from the peak(s) of the liquid-phase components. Peak integration was achieved with a Hewlett Packard 3390 A reporting integrator. Replicated measurements at longer times revealed no increase in the area of the hydrogen peak, indicating that equilibrium absorption was obtained in 10 min. Calibration was achieved by determining the peak areas corresponding to known pressures of hydrogen gas alone in the loop. The plot of peak area vs. hydrogen pressure was highly linear as expected for small quantities of hydrogen in nitrogen carrier gas. Calibrations by injecting pure H_2 at pressure P_c were performed before and after solubility

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Table I. Solubility of Hydrogen in Alcohols and Esters Expressed as Mole Fraction × 10^2 at 291 K and Various Pressures

solvent	pressure, MPa, 10^2 × mole fracn of H_2					
methanol	1.10, 0.18	1.60, 0.26	2.60, 0.44	3.10, 0.52	3.62, 0.61	
methanol[a]	1.51, 0.25	1.70, 0.28	1.81, 0.31	2.08, 0.35	2.19, 0.37	2.61, 0.45
methanol[b]	1.64, 0.19	2.79, 0.32	4.32, 0.49	4.85, 0.55		
methanol[c]	1.76, 0.21	2.71, 0.31	3.31, 0.38	4.55, 0.52		
methyl formate	1.19, 0.26	1.59, 0.35	2.10, 0.44	2.71, 0.50	3.10, 0.71	
methyl formate[b]	2.63, 0.34	3.49, 0.46	4.07, 0.53	4.58, 0.61		
methanol/methyl formate[d]	1.24, 0.25	1.64, 0.33	2.24, 0.45	2.64, 0.55	3.12, 0.62	
ethanol	1.39, 0.31	2.18, 0.50	2.56, 0.57	3.12, 0.67		
1-propanol	1.27, 0.31	1.78, 0.44	2.25, 0.54	3.04, 0.74		
1-butanol	1.52, 0.44	2.15, 0.60	2.60, 0.71	3.10, 0.87		
ethyl formate	1.60, 0.51	2.61, 0.74	3.11, 0.91	4.10, 1.12		
methyl acetate	1.15, 0.30	1.72, 0.43	2.30, 0.57	3.11, 0.78		
ethyl acetate	1.60, 0.61	2.60, 0.95	3.60, 1.23	4.60, 1.55		
1-propyl acetate	1.59, 0.73	2.35, 0.98	3.10, 1.29	4.09, 1.66		
2-propyl acetate	1.31, 0.66	1.80, 0.85	2.38, 1.14	3.04, 1.47		
1-butyl acetate	1.42, 0.60	2.07, 0.84	2.65, 1.09	3.10, 1.40		
methyl propanoate	1.60, 0.68	2.17, 0.88	3.12, 1.23	4.11, 1.43		
methyl butanoate	1.59, 0.88	2.60, 1.23	3.10, 1.43	3.85, 1.73		
methyl 2-methylpropanoate	1.59, 0.87	2.09, 0.98	3.59, 1.56	4.12, 1.97		

[a] Replicate experiment. [b] Method of Albal et al. (*15*). [c] Replicate experiment method of Albal et al (*15*). [d] 50 mol % methanol/50 mol % methyl formate.

measurements for each solvent and showed that detector response was constant.

The mole fraction of hydrogen in each liquid sample was calculated by using the formula

$$X_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_s} \approx \frac{A}{A_c} \frac{P_c M_s}{RT \rho_s} \tag{3}$$

where A and A_c are the areas of the hydrogen peaks for the liquid sample and the calibration gas sample (at pressure P_c) and M_s and ρ_s are solvent molecular weight and density, respectively. The loop volume is not required since it occurs in the calculation of both n_{H_2} and n_s and thus cancels. The formula contains a number of small and partially self-compensating errors (ideal gas assumption for hydrogen, that n_{H_2} is negligible compared to n_s, and that ρ_s is independent of X_{H_2}). However, for the mole fractions used here ($X < 0.02$), the residual error is much less than that intrinsic to gas chromatographic measurements of this type (±2%).

Recently Albal et al. (*15*) have reported the measurement of gas-in-liquid solubility data by a gas absorption technique which involves the measurement of the volumes of the gas and liquid phases and the total pressure change due to gas absorption. The method was developed by Albal et al. (*15*) in order to measure mass-transfer rates where the rate of solute gas uptake by the liquid phase is related to the rate of change in pressure by

$$\frac{-dN_G}{dt} = \frac{V_G}{RT} \frac{dP}{dt} \tag{4}$$

which on integration (equilibrium absorption) yields the concentration of solute in the liquid phase.

$$C_L = \frac{V_G}{V_L} \frac{P_i - P_f}{RT} \tag{5}$$

The mole fraction X_{H_2} is estimated from Henry's law equation

$$P_{H_2} = KX_{H_2} \tag{6}$$

This technique was applied in the current study by using an electronic pressure transducer calibrated to 5 MPa and capable of accurately measuring small pressure changes under high-pressure conditions. The transducer output was measured on a high-speed strip chart recorder.

The alcohols and esters were obtained from Ajax Chemicals Ltd. in 99.8% purity. Hydrogen (99.9%) and nitrogen (carrier gas) were obtained from Commonwealth Industrial Gases Ltd.

Table II. Henry's Law Coefficients (K) for Solution of Hydrogen in Alcohols and Esters and 291 K

solvent	K, MPa
methanol	596 ± 3
methanol[a]	591 ± 4
methanol[b]	879 ± 3
methanol[c]	871 ± 6
methyl formate	453 ± 8
methyl formate[b]	760 ± 5
methanol/methyl formate	495 ± 5
ethanol	452 ± 7
1-propanol	408 ± 3
1-butanol	358 ± 3
ethyl formate	352 ± 9
methyl acetate	399 ± 3
ethyl acetate	289 ± 6
1-propyl acetate	241 ± 5
2-propyl acetate	207 ± 2
1-butyl acetate	233 ± 6
methyl propanoate	265 ± 11
methyl butanoate	214 ± 7
methyl 2-methylpropanoate	214 ± 8

Results and Discussion

The solubility of hydrogen in the different alcohols and esters was measured at pressures in the range 1.1–4.85 MPa at 291 K (Table I). When the pressure of hydrogen (MPa) was plotted against the mole fraction of hydrogen in the liquid phase, excellent linearity was obtained for all systems. This implies that typical dilute solution behavior occurs and allows the use of Henry's law for the calculation of coefficients. These coefficients, calculated for hydrogen dissolved in alcohols and esters, are presented in Table II along with the standard deviations of estimates. The low values of the standard deviations show that the data are well represented by eq 6.

The solubilities of hydrogen in alcohols are compared (on the basis of K values) with literature values in Table III. Our results are in general agreement with most of the previous studies. In particular the values for 1-propanol and 1-butanol agree closely to the values obtained by Brunner (*10*). The value for ethanol is the first reported at pressures above 101.3 kPa other than the statement by Frolich et al. (*4*) that, within experimental error, solubilities in ethanol, 1-propanol, and 1-butanol were identical with the value for 2-propanol (440 MPa) at 298 K and hydrogen pressures up to 19 MPa. The results of this study show that hydrogen solubility increases with increasing molecular weight of the alcohol, a finding similar to that observed for the carbon monoxide/alcohol systems. The sol-

Table III. Henry's Law Constants for Solubility of Hydrogen in Alcohols

alcohol	T, K	P_{max}, MPa	K, MPa	ref
methanol	291	3.62	596	this study
	298	19.0	750	*4*
	298	59.0	682	*5*
	298	82.2	632	*6*
	294	27.6	673	*7*
	273	5.17	303	*8*
	293	0.10	645	*9*[a]
ethanol	291	3.12	452	this study
	298	19.0	440	*4*[b]
	293	0.10	505	*9*[a]
1-propanol	291	3.04	408	this study
	298	9.93	413	*10*
	298	19.0	440	*4*[b]
	298	0.10	427	*9*[a]
1-butanol	291	3.10	358	this study
	298	19.0	440	*4*[b]
	298	9.73	361	*10*
	313	30.4	377	*11*
	298	0.10	375	*9*[a]

[a] Reference *9* is a compilation of literature data which have been smoothed. [b] Based on the statment in ref *4* that, within experimental error, the solubilities in ethanol, 1-propanol, and 1-butanol were the same as for 2-propanol.

Table IV. Henry's Law Constants for Solubility of Hydrogen in Esters

ester	T, K	P_{max}, MPa	K, MPa	ref
methyl acetate	291	3.11	399	this study
	291	0.10	309	*9*[a]
	294	0.10	346	*12*
ethyl acetate	291	4.60	289	this study
	203	0.10	303	*9*[a]
	293	0.10	316	*13*
	294	0.10	304	*14*

[a] Reference *9* is a compilation of literature data which have been smoothed.

ubility data for methyl formate and ethyl formate are important for studies of the carbonylation/hydrogenolysis process for methanol synthesis. The data in Tables I and II are the first published for these esters.

In addition to the interest in the hydrogenolysis of methyl formate and of formates of other alcohol, it has recently been shown (*16*) that many other esters are readily hydrogenated to the parent alcohols. For this reason the solubility of hydrogen in a wide range of acetates was measured and these data are also included in Tables II and IV. A trend similar to that for the alcohols and formates is observed in that the solubility of H_2 increases with the molecular weight of the ester. The data for all the esters are original since previous studies have been confined to methyl acetate (*9*, *12*) and ethyl acetate (*9*, *13*, *14*) at 101.3 kPa.

Table II presents the Henry's law coefficients for methanol and methyl formate determined by using the two experimental techniques described above. Although excellent linearity of liquid-phase concentration of H_2 vs. pressure was obtained by using the method of Albal et al. (*15*), the method significantly underestimates the solubility in both the alcohol (compared with literature values Table III) and the ester. The method described by Tonner et al. (*3*), involving direct measurement of solute concentration in the liquid phase, is considered to be superior to the method of Albal et al. (*15*) which requires accurate measurement of both liquid and gas volumes. Since the hydrogenolysis of methyl formate will yield mixtures of methanol and methyl formate, the solubility of H_2 in an equimolar mixture of methanol/methyl formate was measured. Again excellent linearity was obtained for the plot of H_2 concentration in the liquid phase vs. pressure. The value of K obtained from the plot is 494 MPa (Table II) which is less than the expected value (525 MPa) if ideal behavior applies. Although the system is not ideal, the values of K for methanol and methyl formate are of similar magnitude so that the assumption of ideality should provide data of sufficient accuracy for design purposes.

Glossary

A	area of hydrogen peak in chromatogram for liquid sample
A_c	area of hydrogen peak in calibration sample
C_L	concentration of gas in liquid, mol L^{-1}
M_s	molecular weight of solvent
N_G	number of moles of solute in gas phase
n_{H_2}	moles of hydrogen in sample
n_s	moles of solvent in sample
P	system pressure
P_c	pressure of hydrogen used for calibration
P_f, P_i	final and initial pressure
P_{H_2}	hydrogen pressure, MPa
R	ideal gas constant
T	temperature, K
V_G	gas-phase volume
V_L	liquid-phase volume
x_{H_2}	mole fraction of H_2 in liquid phase
ρ_s	density of solvent

Registry No. CH_3OH, 67-56-1; H_2, 1333-74-0; methyl formate, 107-31-3; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; ethyl formate, 109-94-4; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; 1-propyl acetate, 109-60-4; 2-propyl acetate, 108-21-4; 1-butyl acetate, 123-86-4; methyl propanoate, 554-12-1; methyl butanoate, 623-42-7; methyl 2-methyl propanoate, 547-63-7.

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