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Solubility of CO_2 in Vinyl Acetate and in a Mixture of Vinyl Acetate and Acetic Acid

M. Harustiak* and A. Kaszonyi

Faculty of Chemical Technology, Slovak Technical University, Bratislava 812 37, Czechoslovakia

Solubilities of CO_2 in vinyl acetate and its mixture with acetic acid (1:1 molar ratio) were measured at temperatures from −15 to 0 °C and at pressures from 20 to 100 kPa. Solubilities are characterized by mole fractions of CO_2 and by Henry's constants. The temperature dependence of Henry's constants for vinyl acetate was calculated.

Introduction

In the processes for industrial vinyl acetate manufacturing based on the vapor-phase addition of acetic acid to acetylene, the reaction mixture contains vinyl acetate, acetic acid, acetylene, and a low concentration of CO_2. In the separation steps the vapors are condensed and acetylene is separated from waste gases and recycled. For efficient separation it is necessary to know the solubility of acetylene, CO_2, and other waste gases in pure vinyl acetate or in the so-called "raw vinyl acetate", which is an $x_1 \approx 0.5$ mixture of acetic acid and vinyl acetate. We have published solubility data for acetylene in this system (*1*). The aim of this work was to measure carbon dioxide solubilities in similar mixtures, which are necessary for optimization of acetylene separation. Solubilities of CO_2 were measured at temperatures from −15 to 0 °C and pressures from 20 to 100 kPa.

Experimental Section

The apparatus used for the measurements of CO_2 solubility was a semiflow gas–liquid equilibrium apparatus, described in detail in our previous paper (*1*). The principle of the differential method used is to bring a known additional volume of liquid into contact with a known volume of gas at a given temperature and pressure in the system after obtaining the previous equilibrium among the liquid, its vapor, and the gas at the same temperature and pressure. The change in the gas volume gives the amount of gas dissolved in the added amount of liquid. The temperature of the liquid sample was maintained to ±0.1 °C by circulation of a coolant in the double-walled absorption vessel. Samples of the added liquid were 2–3 mL, and the volume of absorbed gas was measured with a reproducibility of ±0.2 mL. Pressure in the system was measured on a mercury manometer with a reproducibility of ±0.5 mm.

Acetic acid and vinyl acetate were purified by the methods cited by Perrin et al. (*2*) and described in detail in the previous paper (*1*). Commercial grade (99.7%) CO_2 was purified by passing through a concentrated solution of $KMnO_4$, then concentrated sulfuric acid, and then activated carbon. The purified chemicals were analyzed by gas chromatography. Only traces of nitrogen and oxygen were detected by analysis of CO_2 on Porapak N using a TC detector. Vinyl acetate and acetic acid were analyzed on SE-30 using a flame ionization detector (FID). In acetic acid a trace of acetic anhydride was found. The concentration of vinyl acetate was 99.9 wt %. The impurities were acetaldehyde, acetic acid, and divinylacetylene. The liquids were degassed by evacuation and short boiling under low pressure.

Table I. Solubility of CO_2 in Vinyl Acetate

t/°C	P_{tot}/kPa	$x_3 \pm$ SD[a]
0	99.2	0.0308 ± 0.0005
0	66.6	0.0205 ± 0.0003
0	53.3	0.0161 ± 0.0003
0	39.0	0.0109 ± 0.0006
0	24.4	0.0065 ± 0.0001
−5	97.2	0.0367 ± 0.0002
−5	64.0	0.0243 ± 0.0005
−5	50.7	0.0187 ± 0.0005
−5	37.3	0.0137 ± 0.0002
−5	24.0	0.0080 ± 0.0001
−10	99.6	0.0450 ± 0.0005
−10	64.2	0.0283 ± 0.0003
−10	50.8	0.0230 ± 0.0002
−10	37.5	0.0162 ± 0.0001
−10	24.9	0.0103 ± 0.0001
−15	96.0	0.0485 ± 0.0003
−15	64.0	0.0324 ± 0.0005
−15	50.6	0.0251 ± 0.0003
−15	37.6	0.0186 ± 0.0002
−15	29.2	0.0143 ± 0.0002
−15	23.2	0.0110 ± 0.0001

[a] SD = standard deviation from five measurements.

Results

To simplify the treatment of the data, certain assumptions are necessary: (i) the volume change of the liquid sample during saturation is negligible (because it is within the error of reading the gas volume change) and cannot substantially influence the value of the calculated solubility; (ii) CO_2 is an ideal gas at the conditions used.

Mole fractions of CO_2 in vinyl acetate (given as an average value from five measurements) are given in Table I, and mole fractions for the mixture of vinyl acetate and acetic acid are given in Table II. It was found that the plot of total pressure in the apparatus versus mole fraction of absorbed CO_2 is linear. Therefore, Henry's constants (H) for the solubility of CO_2 in vinyl acetate (given in Table III) were calculated by the least-squares method with the equation

$$P_3 = P_{tot} - P_2(1 - x_3) = Hx_3 \tag{1}$$

$$P_{tot} - P_2 = (H - P_2)x_3 \tag{2}$$

where $P_2(1 - x_3)$ represents the partial pressure of the vapor of the liquid sample (*3*). The partial pressures of pure vinyl acetate (P_2) at different temperatures were calculated with the Antoine equation (*4, 5*):

$$\log (P_2/\text{kPa}) = A - B/((t/°\text{C}) + C) \tag{3}$$

where $A = 6.379$, $B = 1320.27$, and $C = 229.19$. The partial

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Table II. Solubility of CO_2 in the $x_1 = 0.5$ Mixture of Acetic Acid and Vinyl Acetate

t/°C	P_{tot}/kPa	$x_3 \pm$ SD[a]
0	90.8	0.0274 ± 0.0004
0	83.0	0.0242 ± 0.0005
0	43.2	0.0123 ± 0.0002
0	29.8	0.0086 ± 0.0002
−5	95.6	0.0337 ± 0.0002
−5	74.5	0.0258 ± 0.0002
−5	47.8	0.0161 ± 0.0004
−5	34.5	0.0113 ± 0.0003
−5	21.2	0.0072 ± 0.0002
−10	92.7	0.0368 ± 0.0004
−10	73.7	0.0291 ± 0.0002
−10	47.0	0.0188 ± 0.0002
−10	33.7	0.0132 ± 0.0002
−10	20.4	0.0074 ± 0.0002
−15	88.3	0.0415 ± 0.0005
−15	56.1	0.0262 ± 0.0005
−15	29.5	0.0132 ± 0.0004
−15	16.1	0.0078 ± 0.0003
−15	9.6	0.0042 ± 0.0002

[a] SD = standard deviation from five measurements.

Table III. Henry's Constants for CO_2 in Measured Liquids

	vinyl acetate		mixture
t/°C	H_{exptl}/kPa	H_{calcd}/kPa	H_{exptl}/kPa
0	3081 ± 49[a]	2936	3280 ± 98[a]
−5	2546 ± 40	2550	2785 ± 50
−10	2163 ± 33	2201	2482 ± 34
−15	1940 ± 12	1887	2108 ± 45

[a] 95% confidence interval (at all temperatures).

pressure at the $x_1 = 0.5$ mixture of vinyl acetate and acetic acid could not be calculated by the above-mentioned method because of the nonideality of the mixture. Even for the low temperature used, the errors caused by nonideality should not be ignored (*3*). This value is supposed to be constant at constant temperature and constant composition of the liquid. So, Henry's constants for the mixture could be calculated from the linear dependence of the total pressure in the system versus x_3 with the equation

$$P_{tot} = P_M + (H - P_M)x_3 \tag{4}$$

where P_M is an unknown but constant parameter, which is for such a low temperature negligible in relation to Henry's constants.

The temperature dependence of Henry's constants for pure vinyl acetate was fitted by the equation recommended by Prausnitz et al. (*6*):

$$H_{calcd} = f\Gamma \tag{5}$$

where $\Gamma = \exp(a_0 + a_1/T)$ is the activity coefficient and $f = \exp(7.224 - 7.534T_c/T - 2.598 \ln(T/T_c) + \ln P_c)$ is the fugacity. The parameters $a_0 = 6.3$ and $a_1 = -476.5$ were calculated from experimental values of Henry's constants (H_{exptl}) by the least-squares method. H_{exptl} are compared with H_{calcd} in Table III.

Glossary

H	Henry's constant for CO_2
P_c	critical pressure of CO_2
P_i	partial pressure of compound i
P_{tot}	total pressure in apparatus
t,T	temperature
T_c	critical temperature of CO_2
x_i	mole fraction of compound i

Subscripts

1	acetic acid
2	vinyl acetate
3	CO_2
M	mixture of vinyl acetate and acetic acid with $x_1 = 0.5$

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