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

A. Kaszonyi,* M. Harustiak, and J. Kizlink

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

Solubilities of acetylene 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 acetylene and by Henry's constants. The temperature dependence of Henry's constants for vinyl acetate was calculated, too.

Introduction

One of the processes for industrial vinyl acetate manufacturing is based on the vapor-phase addition of acetic acid to acetylene which is catalyzed by a heterogeneous catalyst. The reaction mixture contains vinyl acetate, acetic acid, acetylene, and a low concentration of CO_2. In the separation steps, vapors are condensed and acetylene is separated from waste gases and recycled.

For efficient separation it is necessary to know the solubility of acetylene 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. Solubility data for acetylene in such systems are available at temperatures from 0 to 40 °C (*1*, *2*), but industrial absorbers operated at lower temperatures are more effective. Solubilities were measured at temperatures from −15 to 0 °C and pressures from 20 to 100 kPa.

Experimental Section

The apparatus used for the solubility measurements was a semiflow gas–liquid equilibrium apparatus (Figure 1). The principle of this differential method 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 equilibrium between the initial liquid, its vapors, and the gas at the same temperature and pressure. Equilibrium is attained by agitation of the system for some time until no change in the volume of the gas is observed. The change in gas volume gives the amount of gas dissolved in the added amount of liquid.

The experimental technique used in this work is similar to that used by Haimour and Sandall (*3*), with the following modifications: The mixing of liquid and gas was performed with a magnetic stirrer. The temperature of the liquid sample was checked by thermometer in the absorption flask and maintained to ±0.1 °C by circulation of cooling media in the double-walled absorption vessel. The system was first purged with acetylene for a few minutes and then evacuated. This step was repeated three times. The working pressure of absorbed gas was adjusted within the range of 20–100 kPa and checked by measuring of the distance between mercury levels in the measuring branches. A small amount (2–3 mL) of degassed vinyl acetate or its mixture with acetic acid was then injected into the absorption vessel and mixed for 20–30 min at the desired temperature and pressure. The equilibrium between the liquid, its vapors, and the absorbed gas was determined by no changes in the volume of absorbed gas at adjusted pressure. The equilibrium was checked by changing the pressure by 5–10 mmHg for a few minutes and returning to the initial pressure. The change in the volume of absorbed gas was within the reproducibility of the method (±0.2 mL). A new sample of liquid was then added, and the technique described above was used. Adequate rising of the mercury reservoir was necessary to keep the pressure constant. The distance between the mercury levels was measured with the reproducibility of ±0.5 mm. The volume of absorbed gas is the measured volume change plus the volume of liquid sample.

The accuracy of the experimental method and apparatus was checked by measuring the solubility of acetylene in distilled water at a temperature of 20 °C and a pressure of 1 atm. We found a solubility of 1.22 ± 0.03 g/kg, which is very close to the published value of 1.23 g/kg (*4*).

Acetic acid and vinyl acetate were purified by the methods cited by Perrin et al. (*5*). Acetic anhydride and CrO_3 were added to acetic acid, and then the mixture was heated for 1 h to just below boiling. The fraction from 118.1 to 118.2 °C was separated by fractional distillation. Vinyl acetate was dried with $CaCl_2$, and then the fraction from 72.5 to 72.7 °C was separated by fractional distillation under nitrogen and stabilized by a small amount of hydroquinone (4 ppm). The mixture prepared from vinyl acetate and acetic acid was of 1:1 molar ratio. Commercial grade (99%) acetylene was purified by being passed through concentrated sulfuric acid, then solid NaOH, and then activated carbon. The liquids were degassed by evacuation and short boiling under low pressure.

The purified chemicals were analyzed by gas chromatography. Only traces of methane, acetone, and nitrogen were detected by analysis of acetylene on Porapak N using TCD. 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 %. Impurities were acetaldehyde, acetic acid, and divinylacetylene.

Results

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

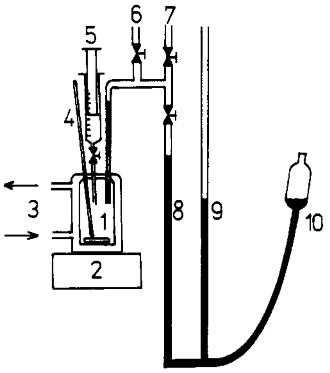

Figure 1. Solubility apparatus: (1) absorption flask; (2) magnetic stirrer; (3) circulation of cooling medium; (4) thermometer; (5) liquid sample injector; (6) vacuum; (7) acetylene; (8) buret; (8,9) measuring branches; (10) mercury reservoir.

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Table I. Solubility of Acetylene in Vinyl Acetate

t/°C	P_{tot}/kPa	$X_3 \pm$ SD[a]
20	101.0	0.0345 ± 0.0002
20	80.6	0.0286 ± 0.0004
20	53.9	0.0170 ± 0.0003
20	40.6	0.0098 ± 0.0008
0	101.4	0.0580 ± 0.0001
0	81.4	0.0482 ± 0.0009
0	68.1	0.0404 ± 0.0005
0	54.7	0.0312 ± 0.0002
0	41.4	0.0229 ± 0.0004
0	28.1	0.0137 ± 0.0004
−5	94.2	0.0727 ± 0.0007
−5	74.5	0.0565 ± 0.0008
−5	61.2	0.0451 ± 0.0009
−5	47.8	0.0358 ± 0.0002
−5	34.5	0.0253 ± 0.0002
−10	99.7	0.0824 ± 0.0003
−10	79.6	0.0658 ± 0.0005
−10	66.3	0.0549 ± 0.0004
−10	53.0	0.0450 ± 0.0003
−10	39.6	0.0313 ± 0.0005
−15	96.2	0.0950 ± 0.0003
−15	75.5	0.0738 ± 0.0005
−15	62.2	0.0602 ± 0.0004
−15	48.8	0.0466 ± 0.0005
−15	35.5	0.0332 ± 0.0007
−15	22.2	0.0212 ± 0.0008

[a] SD = standard deviation from five measurements.

Table II. Solubility of Acetylene in the X_1 = 0.5 Mixture of Acetic Acid and Vinyl Acetate

t/°C	P_{tot}/kPa	$X_3 \pm$ SD[a]
0	100.3	0.0520 ± 0.0004
0	80.0	0.0392 ± 0.0005
0	66.7	0.0320 ± 0.0005
0	53.4	0.0257 ± 0.0004
0	40.0	0.0190 ± 0.0003
0	26.7	0.0120 ± 0.0002
−5	97.2	0.0589 ± 0.0009
−5	76.9	0.0472 ± 0.0005
−5	63.6	0.0386 ± 0.0008
−5	50.3	0.0301 ± 0.0004
−5	36.9	0.0221 ± 0.0002
−5	23.6	0.0133 ± 0.0003
−10	96.6	0.0613 ± 0.0008
−10	76.4	0.0479 ± 0.0009
−10	63.0	0.0392 ± 0.0009
−10	49.7	0.0284 ± 0.0008
−10	36.4	0.0206 ± 0.0006
−10	23.0	0.0122 ± 0.0006

[a] SD = standard deviation from five measurements.

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

	vinyl acetate		mixture
t/°C	H_{exp}/kPa	H_{cal}/kPa	H_{exp}/kPa
20	2492 ± 190[a]	2505	
0	1632 ± 47	1538	1950 ± 64[a]
−5	1261 ± 18	1344	1562 ± 27
−10	1172 ± 24	1166	1470 ± 27
−15	1001 ± 10	1006	

[a] 95% confidence interval at all temperatures.

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

$$P_3 = P_{tot} - P_2 = HX_3 \tag{1}$$

The partial pressures of vinyl acetate (P_2) at different temperatures were calculated with the Antoine equation (*6*, *7*).

$$\log (P_2/\text{kPa}) = A - B/((t/°\text{C}) + C) \tag{2}$$

where A = 6.379, B = 1320.27, and C = 229.19.

For the X_1 = 0.5 mixture of vinyl acetate and acetic acid, the Henry's constants were calculated from the linear dependence of P_{tot} versus X_3.

The temperature dependence of the Henry's constants for vinyl acetate was fitted by the equation

$$H_{cal} = f\Gamma \tag{3}$$

where (*8*) $\Gamma = a_0 + a_1/T$ and $f = \exp(7.224 - 7.534T_c/T - 2.598 \ln (T/T_c) + \ln (P_c))$, with a_0 and a_1 calculated from experimental values of Henry's constants (H_{exp}) by the least-squares method. H_{exp} are compared with H_{cal} in the Table III.

Glossary

H	Henry's constant for acetylene, kPa
P_c	critical pressure of acetylene, kPa
P_i	partial pressure of compound i, kPa
P_{tot}	total pressure in apparatus, kPa
t	temperature, °C
T	temperature, K
T_c	critical temperature of acetylene, K
X_i	mole fraction of compound i

Subscripts

1	acetic acid
2	vinyl acetate
3	acetylene

Registry No. Acetylene, 74-86-2; vinyl acetate, 108-05-4; acetic acid, 64-19-7.

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