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THE SOLUBILITY OF CARBON MONOXIDE IN SOME LOWER MONOVALENT ALCOHOLS

BY

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KØBENHAVN I KOMMISSION HOS EJNAR MUNKSGAARD 1948 In an earlier paper (1) on the reaction velocity in the process between carbon monoxide and methyl- and ethyl alcoholate dissolved in the corresponding alcohols the solubility of carbon monoxide in these alcohols entered into the calculation of the velocity constant. A final calculation of the experiments was impossible owing to the lack of data on the solubility of carbon monoxide between 20° and 50° . The present paper deals with this solubility in methyl-, ethyl-, normal propyl- and isopropyl alcohol as well as in normal butyl- and isobutyl alcohol at the lemperatures in question.

The solubility of carbon monoxide in methyl- and ethyl alcohol has previously been investigated by CARIUS (2), JUST (3) and SKIRROW (4), and a review of the results is given in Table 1. But the literature, as far as the author is aware, does not contain any data on the solubility of carbon monoxide in the propyland butyl alcohols. The solubilities recorded in Table 1 are expressed by means of Ostwald's absorption coefficient, i. e. the ratio between the concentration of the gas in the saturated solunon and the concentration of the gas in the gas phase. CARIUS expresses the solubility of carbon monoxide in ethyl alcohol by means of Bunsen's absorption coefficient as 0.204 from 0° to 25°; this is in the table converted according to Ostwald's absorption coefficient.

Table 1.

Solubility (l = Ostwald's absorption coefficient) of carbon monoxide in alcohols.

	CH	30H	C ₂ H ₅ OH		
	20°	25°	20°	25°	
arius, 1855	0,1830	0.1955	0.219 0.1901	0.223 0.1921	
kiriow, 1902		0.196		0.192	

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Apparatus.

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The solubility determinations described in the present paper were carried out in an apparatus which in principle is first described by ESTREICHER (5) and later improved by LANNUNG (6), whose paper on the subject contains a sketch and a detailed description. The particular advantage of the apparatus is that the experimental space is shut off by mercury, so that neither gas nor solvent during the experiment comes into contact with stopcocks and stopcock grease. During the experiment the ap paratus was constantly shaken in an air thermostat the temperature of which between 20° and 50° could be kept constant with an accuracy of about 0.05° .

The procedure followed in the solubility determinations is described in detail by LANNUNG in the paper cited. In principle it is as follows: After the apparatus is completely filled with mercury a suitable volume of alcohol (about 20 ml) is sucked in and freed from air by keeping the apparatus evacuated for about 12 hours with repeated suction and shaking, whereupon the alcohol is confined between two mercury surfaces. Next about 6 ml of carbon monoxide is sucked into another part of the apparatus where it likewise is confined between mercury surfaces. The apparatus is now placed in the thermostat at 20° and the volume and pressure of the carbon monoxide read after tem. perature adjustment. Then the carbon monoxide is brought into contact with the alcohol by the separating string of mercury being allowed to drop down into the alcohol. The shaking is started and continued until the manometer reading shows no change los at least half an hour. Then the equilibrium adjustment is carried out at different temperatures. Finally the volume of liquid determined by weighing the amount of mercury that can be drawn to a calibration mark. The volume of the manometer tube of the apparatus and the volume between the various marks and determined by weighing with mercury.

Materials.

Methyl-, ethyl-, and normal propyl alcohol were dehydrate in an apparatus made completely of glass, magnesium being use according to H. LUND and J. BJERRUM (7). It was attempted to dehydrate isopropyl alcohol by the same method, but magnesium could not be made to react with this alcohol. The dehydration of isopropyl alcohol, normal butyl- and isobutyl alcohol was accomplished by slow distillation in a wire-gauze column (8) with 50 plates. Table 2 presents a summary of the boiling points



Fig. 1. S: Formic acid. K: Sulphuric acid. A: Sodium hydroxide solution. B: Sulphuric acid. C: Cotton-wool filter. G: Gasometer with mercury. N: Levelling container.

and densities found, the last two columns giving the corresponding constants from the literature. The boiling points were determined by distillation of 20 ml of alcohol in a boiling point apparatus described by H. BAGGESGAARD RASMUSSEN and F. REIMERS (9). calibrated thermometers were placed so that the whole mercury column was in alcohol vapour. The boiling points are converted 760 mm pressure. The densities were determined at $20.^{\circ}00 \pm$ 02° in a 50 ml pycnometer with two graduated capillary tubes provided with ground-glass caps. In the calculation of the density porrection is made for the buoyancy of the air.

Carbon monoxide was prepared in an apparatus like the one etched in Fig. 1. From the separating funnel (S) anhydrous whic acid dripped into concentrated sulphuric acid in the flask b. The carbon monoxide was led through glass spiral washing Nr. 13

bottles containing sodium hydroxide solution (A) and concentrated sulphuric acid (B) and a cotton-wool filter (C) into a 500 ml Berzelius gasometer (G) with levelling container (N). The carbon monoxide production was made very slow so that the washing could be effective. The gasometer was filled and emptied until sampling (stopcock D) showed that the carbon monoxide was pure. The analyses were carried out in a gas analysis apparatus according to J. A. CHRISTIANSEN (10); the gas employed contained 99.5 % carbon monoxide and 0.5 % nitrogen (no carbon dioxide nor any oxygen).

			Table 1	2.			
Boiling	points	and	densities	\mathbf{of}	the	alcohols	used.

01				3	
·	· Fo	und	Values from literature11, 18		
Alcohol CH_3OH C_2H_5OH $n-C_3H_7OH$ $i-C_3H_7OH$ $i-C_4H_9OH$	$\begin{array}{c c} \text{Boiling point.} \\ \hline 760 \text{ mm} \end{array} \begin{array}{c} \text{Density} \\ \frac{20}{4} \end{array}$		Boiling point 760 mm	$\frac{\text{Density}}{d\frac{20}{4}}$	
		·			
СН ₃ ОН	64.7	0.7916	64.7	0.7914	
C.H.OH	78.3	0.7892	78.3	0.7893	
n-C-H-OH	97.2	0.8038	97.2	0.8034	
i-C H-OH	82.4	0.7859	82.4	0.7854	
~ C U OH	117.8		117.7		
	107.0	Į	107.9		
$1-G_4H_9OH$	107.9		1 101.9		

Experimental results.

The densities and vapour pressures used in the calculations are given in Table 3. The solubilities are expressed by Ostwald's absorption coefficient (1) and calculated from

$$\mathbf{l} = \frac{(\mathbf{W} - \mathbf{w}) \cdot 760 \cdot \mathbf{T}}{\mathbf{W}_{\mathbf{L}} \cdot \mathbf{P} \cdot 273.1},$$

where W is the volume $(0^{\circ}, 760 \text{ mm})$ of the gas introduced, the volume $(0^{\circ}, 760 \text{ mm})$ of the gas that remains after the ab sorption. W_L is the volume of the alcohol and P the partial pressure of the carbon monoxide, both at the prevailing absolut temperature T. The following survey shows an example of the calculation of the solubility of carbon monoxide in ethyl alcohol:

	Before the absorption	After the absorption
Temperature t ^o C	19.97°	19.97°
273.1	1.0732	1.0732
Total pressure in the container	749.3 mm Hg	746.9 mm Hg
Fressure of C_2H_5OH at 19.97°	44.0	44.0
Partial pressure of CO p _{CO}	= 705.3	P = 702.9
volume of CO at 19.97° and p_{CO} .	6.721 ml	3.901 ml
0° and 760 mm .	5.812 -	w = 3.362 -

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The flask could hold 1189.0 g mercury, and a total of 997.3 g Hg was drained off at 20° (density of Hg 13.546), thus

$$W_{L} = \frac{1189.0 - 997.3}{13.546} = 14.15 \text{ ml} \qquad \text{and}$$
N's absorption coefficient $\alpha = \frac{(5.812 - 3.362) 760}{14.15 \cdot 702.9} = 0.1872$
LD's $- l = 0.1872 \cdot \frac{273.1 + 19.97}{273.1} = 0.2009$

$$l_{20.0^{\circ}} = 0.201.$$

Table 3.

alues of densities and vapour pressures of the alcohols used in the calculations.

	Temp.	СН _а ОН	C ₂ H ₅ OH	n-C ₃ H ₇ OH	i-C ₃ H ₇ OH	n-C ₄ H ₉ OH	i-C₄H9OH
a 4	20.0 30.0 40.0 50.0	0.7915 0.7825 0.7740 0.7650	0.7894 0.7810 0.7722 0.7622	0.8035 0.7960 0.7875	0.7851 0.7769 0.7686	0.8098 0.8026 0.7954	0.8018 0.7941 0.7864
	Lit.	(13)	(13)	(13)	(12)	0.7882 (12)	0.7785 (12)
BH um	20.0 30.0 40.0 50.0 Lit.	95.1 160.3 260.4 409.4 (13)	44.0 78.1 133.4 219.8 (13)	14.5 27.6 50.2 87.2 (12)	32.4 59.1 105.6 176.8 (14)	4.39 9.52 18.6 33.7 (12)	8.6 17.0 31.6 56.2 (15)

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In the numerical treatment of the experiments at other ten perature equilibrium. As Table 5 shows, the two apparatuses gave portion to the experimental errors.

Tables 4-9 show the solubilities found. Values in the same carbon monoxide. The experiments with methyl alcohol (Tables even provided the present of the coefficients.

were difficult to reproduce, undoubtedly because of the ver high vapour pressure. At 20° l was found to be 0.224, thus value about 23% higher than that found by JUST (Table 1 An experiment with methyl alcohol to which had been adde $1^{0/0}$ of water gave at $20^{\circ} l = 0.220$. When the carbon monoxid pressure was varied the following values were found for t solubility in anhydrous methyl alcohol at 20°: 538 mm (0.22) 680 mm (0.224), 754 mm (0.224), thus the same within the example 1perimental accuracy. The difference between Just's results and those of the present investigation may perhaps be explained by the circumstance that different values of the vapour pressure methyl alcohol have been used. JUST found that the solubility between 20° and 25° rises 0.0021 per degree, while the prese experiments give a rise of 0.0008 per degree. A comparison Just's temperature coefficient with the temperature coefficient for the solubility of carbon monoxide in the other alcolo (Table 10) shows Just's coefficient to be incredibly high.

For the solubility of carbon monoxide in ethyl alcohol (Tal 5) I was found to be 0.200 at 20°, thus a value lying between those found by CARIUS and JUST (Table 1). The experiment reported under "Apparatus A" were carried out in an apparate having a flask volume of about 300 ml. About one year lat (a new dehydrated alcohol and a newly prepared carbon mononed being used) experiments were made in "Apparatus B", will flask volume of about 90 ml. Since only less than 20 ml of alcou can be introduced because of the high solubility, and the of the flask is filled with mercury, Apparatus B makes the melli so much more rapid and more satisfactory in producing to

peratures consideration was given to the various alcohol vapor the same value for the solubilities. In the case of the other alcohols pressures and to the coefficients of expansion of the alcohol only Apparatus B has been used. Ethyl alcohol with 1% of the mercury and the glass. The alcohol vapour pressures we water gave l = 0.190 at 20°. From CARIUS' results one arrives not corrected for the reduction which is attributable to the defat a temperature coefficient of 0.0007. Just's results give no solved carbon monoxide, nor was the volume of the alcohoreliable temperature coefficient (0.0004) since the deviations of the corrected for changes due to evaporation or to carbon monoxid solubilities found are so small. The present experiments show an dissolved. The three last mentioned corrections are small in presidence in solubility of 0.00053 per degree, which is of the same order of magnitude as for the rest of the alcohols investigated.

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Table 10 presents a survey of the solubilities found, intervertical column originate from the same charge of alcohol an polated to the temperatures 20°, 35° and 50°, as well as the cor-

Table 4. Solubility in methyl alcohol.

t	1	1	1
19.9	0.226		
20.0	0.220		0.222
20.1		0.224	
29.0	0.225		
$34.2\ldots$		0.236	
35.2			0.228
39.5	0.233		
49.8	0.241		0.250

Table 5. Solubility in ethyl alcohol.

Apparatus A			Apparatus B			
, t]	· 1,	t	1	1	
.0	0.200	0.200 0.206	20.0	0.201	0.203	
1.0	0.210	0.208	20.7 28.9	0.201* 0.204		
	0.215		29.8 33.7	0.208*	0.206	
			37.9 38.8	0.211	0.211	
			50.2	0.214	0.217	

The equilibrium entered from higher to lower temperature.



0.00030

0.00040

ontal axis. Integration of the equation for the temperature decendence of the solubility, $\frac{d\ln l}{dT} = -\frac{u}{RT^2}$, where u is the heat solution, gives, for constant u:

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$$\ln l = \frac{u}{1.986 \cdot T} + \ln a$$
, or $\log l = \frac{u}{4.57 \cdot T} + \log a$

ne constants u and log a in the last equation are calculated by nears of the method of least squares, Table 11. The calculation

Discussion.

0.169

0.180

0.173

0.186

0.164

0.174

n-C₄H₉OH

i-C₄H₉OH

Fig. 2 shows corresponding values of $\frac{1}{T} \cdot 10^5$ (abscissae) and log l (ordinates). The degrees centigrade corresponding to the reciprocal absolute temperature are plotted on the upper home

is also carried out in the case of methyl alcohol where the points fall on a straight line.

The solubility being found to be increasing with rising in isocompounds than in the normal compounds. temperature is in agreement with a theory for the temperature dependence of the solubility of gas proposed by TAMMANN (16)





In Fig. 3, u (abscissae) is plotted against log a (ordinates) Assuming linear dependence, the equation

$$\log a = -\frac{u}{837} - 0.94$$

is calculated and the straight line drawn. LANNUNG (6) found on an average for the solubility of eight gases (He, Ne, A, Re H₂, CO, CO₂) in methyl alcohol, ethyl alcohol, acetone, cycl hexane and cyclohexanol the equation:

$$\log a = -\frac{u}{3000} - 0.3.$$

When comparing the solubility of gases in different liquid it is the most reasonable to express the solubility in mol fraction (x) which for sparingly soluble gases can be calculated from

$$x = \frac{1 \cdot 273.1 \cdot \text{molecular weight}_{alcohol} \cdot 10^{-1}}{T \cdot 22.4 \cdot d_{T (alcohol)}}$$

Expressed by x the solubility of carbon monoxide at 20° is possibly because of the smaller experimental accuracy, do not recorded in Table 12. x is found to increase with rising molecular weight of the alcohols and is found to be greater

Table 11.

Values of u and log a in the equation $\log l = \frac{u}{R_{\star}T} + \log a$.

Alcohol	u [%]	log a
$CH_{3}OH \dots C_{2}H_{5}OH \dots C_{2}H_{5}OH \dots I_{1}C_{3}H_{7}OH \dots I_{1}C_{3}H_{7}OH \dots I_{1}C_{4}H_{9}OH \dots I_{$	$ \begin{array}{r}630 \\483 \\410 \\506 \\334 \\419 \\ \end{array} $	$0.18 \\0.34 \\0.45 \\0.35 \\0.54 \\0.45$

Table 12.

Solubilities of carbon monoxide expressed in mol fraction $(x \cdot 10^4)$ at 20° and some related constants for the alcohols.

94. 	x • 104	μ	ДH	⊿E	v	$\frac{\Delta E}{v}$	$\alpha \cdot 10^{24}$
СН ₃ ОН	3.77	1.6	8520	7850	40.5	8010	3.24
_C ₂ H₅OH	4.85	1.71	9580	8882	58.3	6240	5.04
n-C₃H₂OH	5.50	1.66	9840	9105	74.8	5040	6.90
i-C₃H7OH	6.10	1.70	9550	8844	76.5	4790	6.91
nC₄H₀OH	6.24	1.66	10450	9674	91.5	4380	8.72
i-C₄H₀OH	6.69	1.8	10220	9464	92.4	4250	8.74

Dipole moment in Debye; Δ H: Heat of vaporization in $\frac{\text{cal}}{\text{mol}}$; Δ E: Energy of apprization in $\frac{\text{cal}}{\text{mol}}$ (= Δ H -- RT); v: Molecular volume in ml; $\frac{\Delta E}{v}$: "Internal in atm.; a: Polarizability calculated from molecular refractivity (R), Values from Intern. Crit. Tables and Landolt-Börnstein's Tables. 47N

Table 12 moreover records the dipole moments (μ) , heats vaporization (Δ H), molecular volumes (v), and polarizabilities) of the alcohols. Moreover, $\frac{\Delta E}{v}$ has been calculated (see the ble), presumably giving quite valuable information regarding relative internal pressures in the alcohols which are almost Nr. 13 Nr. 13

Table 13. Solubility of different gases in the alcohols expressed in mol fraction $(x \cdot 10^4)$ at 20°. Ar at 0°.

	He ⁶)	Ne ⁶)	Ar ¹⁸)	Rn ²⁰)	$H_{2}{}^{3}$)	N ₂ ³)	$O_2^{21})$	со	CO3	N ₂ 0 ²¹
$\begin{array}{c} ``Ideal''^{*} \dots \\ CH_{3}OH \dots \\ C_{9}H_{5}OH \dots \\ n-C_{3}H_{7}OH \dots \\ i-C_{9}H_{7}OH \dots \\ n-C_{4}H_{9}OH \dots \end{array}$	0.57 0.73	1.7 0.78 1.05	21 4.8 6.5 7.3 8.6	710** 94 170 266 215 338	$1.5 \\ 2.1$	10 2.3 3.4	16 3.1 3.7	11 3.77 4.85 5.50 6.10 6.24	178 60 ²²) 69 ²²) 77 ³)	202 55 72

* Calculated by HILDEBRAND (17).** Calculated by the author.

identical in polarity. Carbon monoxide belongs to the non-pola gases (dipole moment 0.12 Debye (11)). The fact that the solubility is found to increase with decreasing internal pressure is in agree ment with a long series of earlier observations (see, for example a review of the solubility of non-polar gases in different liquids on p. 134 of HILDEBRAND'S monograph (17)). The fact that the solubility varies in the same manner as the polarizability is in agreement with a series of observations by SISSKIND and KASAR NOWSKY (18).

DOLEZALEK (19) has shown that for a number of liquid mix tures of two non-electrolytes, A and B, (e. g. benzene and ethylene chloride) one finds for the whole range of concentration that

$p = p_0 \cdot x$,

where p is the partial pressure of A (B), p_0 the vapour pressur of pure A (B) and x the concentration of A (B) calculated mol fraction. If one of the components is associated (e. g. C6) in benzene), or the components enter into additive combination with each other (e. g. acetone and chloroform), this circumstane must be taken into account in the calculation of x. On the bas of the following considerations, DOLEZALEK has proposed method for calculating the ideal solubility of gases in liquid A liquid which is saturated by a gas of the partial pressure can be imagined to be formed by mixing into the liquid so mu "liquid gas" that the mixture has a partial pressure of the ga

of the magnitude p. The solubility of the gas given at a partial pressure of one atmosphere then is

solubility
$$= x = \frac{1}{p_0}$$

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where p_0 is the vapour pressure of the gas in liquid form at the temperature considered.

Most of the gases for which solubility measurements are available have critical temperatures considerably below the temperature at which the solubility determinations have been carried out. HILDEBRAND (17) has, however, for a number of gases calculated theoretical solubilities according to the above equation by extrapolating available vapour pressure measurements of the condensed gases to 20°. Some of the results of these calculations are reproduced in Table 13. The solubility of radium emanation has by the present author been calculated on the basis of vapour pressure measurements by GRAY and RAMSAY (23), by interpolating to a vapour pressure at 20° of 14.1 atmospheres, whence $x = \frac{1}{14.1} = 0.0710$. This calculation of solubilities is thus very

approximate, but nevertheless gives a fair orientation regarding the relative magnitude of these quantities. This "ideal solubility", x, is independent of the solvent. In practice the solubilities are most generally found to depend on the solvent, and as a rule to be between one and ten times as small as the "ideal" one, though for the solubility in water one as a rule finds that it is about one hundred times smaller.

Table 13 surveys the solubility of different one-, two-, and three-atomic gases in six alcohols. The values are inter- or extrapolated to 20° and converted into mol fraction.

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Summary.

The solubility of carbon monoxide between the temperature 20° and 50° is determined in methyl-, ethyl-, normal propylisopropyl-, normal butyl-, and isobutyl alcohol. The results are expressed by means of Ostwald's solubility coefficient (1) and recorded in Table 10, where also dl/dt is calculated. A graphical presentation of the measurements is given in Fig. 2. Within the experimental accuracy the points found lie on a straight line for the equation of which $(\log l = \frac{u}{R \cdot T} + \log a)$ the constants u and log a are calculated in Table 11.

Table 12 gives the solubility expressed in mol fraction $(x \cdot 10^4)$ This table also includes a calculation of the ratio between the energy of vaporization and the molecular volume for each alcohol $\frac{\Delta E}{v}$, which for the alcohols almost identical in polarity furnishes information regarding the relative internal pressure. It will be

seen that the solubility of carbon monoxide increases with falling internal pressure for the alcohols, which rule is in agreement with that governing the solubility of other gases in various solvents

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