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The Solubility of Carbon Dioxide in Perfluoro-*n*-heptane, Normal Heptane, *Cyclo*-hexane, Carbon Tetrachloride, Benzene, Carbon Disulphide and Aqueous Solution of Aerosol

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In three recent papers dealing with the solubility of nitrogen [1], chlorine [2], hydrogen, oxygen and carbon monoxide [3] in non-polar solvents, it was shown that it is possible to account for the solubility by theories based upon a model process of mixing two liquids. The calculation of the solubility was, in the case of chlorine, carried out using heats of vaporization and molal volumes for chlorine and for the solvents. In the case of gases having low solubility (nitrogen, hydrogen, oxygen, carbon monoxide) the solubility parameters for the gases were empirically adjusted.

It is the purpose of this paper to investigate whether it is possible without empirical adjustment to account for the solubility of carbon dioxide which is another gas of relatively high solubility and for which we have all necessary physical data. We would expect the linear carbon dioxide molecule to obey the equations which are valid for mixtures in which association and formation of chemical compounds are absent. Contrary to chlorine, carbon dioxide is at room temperature close to its critical temperature (31° C) and it was difficult in advance to know whether this fact would influence the calculation of the solubility.

APPARATUS, MATERIALS AND PROCEDURE

The solubility determinations were carried out in the same apparatus and using the same procedure as described in a previous paper [3].

Carbon dioxide was prepared by adding concentrated sulphuric acid to potassium bicarbonate (analytical reagent, Judex). After being passed through concentrated sulphuric acid the carbon dioxide was collected in an all-glass gasometer consisting of two one liter flasks placed beside each other, and in the bottom connected with glass tubing about 20 cm long and 1 cm in diameter. The carbon dioxide was analysed by absorption in 35 per cent potassium hydroxide in a gas analysis apparatus as devised by Christiansen[4]. When analysis showed a content of less than 0.1 per cent impurities the gas was regarded as pure. It appeared that the carbon dioxide in the gasometer was gradually contaminated with atmospheric air which, presumably, was diffused through the concentrated sulphuric acid in the gasometer. In the course of three weeks the gas contained about two per cent atmospheric air. The gas employed was in most experiments 99.9 per cent CO_2. In experiments carried out with gas containing a greater amount of impurity (until 0.5 per cent) the solubility measurements were converted by a method as described below.

The solvents used were all purified by fractionation in a wire-gauze column. The employed perfluoro-*n*-heptane (C_7F_{16}), *n*-heptane, benzene and carbon disulphide were of the same purity as described in the previous paper[3]. Carbon tetrachloride (analytical reagent, Riedel-E. de Haën) showed boiling point 76.80° C at 759 mm and refractive index $n_D = 1.4573$ at 25° C. *Cyclo*-hexane purified by fractionated freezing, dried by phosphorous pentoxide and distilled, showed boiling point 80.69° C—80.71° C at 760 mm and freezing point 6.2—6.4° C. The solution of aerosol was a 0.15 per cent aqueous solution of aerosol OT 100 % (dioctylester of the sodium salt of sulphotartaric acid, Amer. Cyanamid Co.). In the solution pH was 7.4.

Values for vapour pressures and densities used in the calculation of the solubility experiments are given in Table 1 in the previous paper[3]. Further, the vapour pressure and density of carbon tetrachloride at 25° C equal 114.5 mm[5] and 1.5843[5], respectively, was used. For the vapour pressure of the aerosol solution at 25° C the value valid for pure water (23.8 mm) was used.

Since carbon dioxide in the solvents used is considerably more soluble than oxygen and nitrogen even small amounts of impurity of atmospheric air will cause an essential error in the solubility determinations. The error depends on the amount of impurity as well as on the volume of the gas before and after absorption has taken place. A calculation, originating from an experiment on the solubility of "carbon dioxide" (99.5 per cent CO_2, 0.5 per cent atm. air) in 8.54 ml water at 25° C, is given in the following.

The volume before absorption was 6.647 ml (0°, 760 mm) corresponding to a content of 0.0352 ml atmospheric air. After the absorption had taken place the reduced volume of the gas was 0.970 ml (corresponding to 1.170 ml at 25° C and $p = 687.9$ mm), *i.e.* the pressure of the carbon dioxide has been about $\frac{0.0332}{0.970}\,100 = 3.4$ per cent less than one atmosphere. Making allowance for the small amount of atmospheric air which has been dissolved in the water we calculate that the pressure of carbon dioxide after equilibrium has taken place is $\frac{0.0284}{0.970}\,100 = 2.9$ per cent less than one atmosphere. If we calculate the solubility ignoring the impurity (0.5 per cent) we get $\alpha = 0.733$. Adding to this value 2.9 per cent we get $\alpha = 0.754$. An experiment carried out with pure carbon dioxide (99.997 per cent) resulted in the value $\alpha = 0.754$.

EXPERIMENTAL RESULTS

The results of the solubility determinations have been reproduced in Table 1, expressed as Bunsen absorption coefficient (α), *i. e.* the number of ml of the gas reduced to 0° C and 1 atm. which can be dissolved in 1 ml solvent at the temperature concerned when the partial pressure of the gas is 1 atm. By converting the experiments into a partial pressure of 1 atm. carbon dioxide has been considered to obey Henry's law. That this is correct at pressures approximately 1 atm. appears from Table 1, where the partial pressures of carbon dioxide in the equilibrium are stated. Even at five atmospheres Hähnel[7] found for the solubility of carbon dioxide in water only about eight per cent deviation from Henry's law at 15° C.

According to Horiuti[8] one ml of carbon tetrachloride will expand 0.00215 ml for each ml carbon dioxide dissolved at 25°. At a one atmosphere partial pressure of carbon dioxide the carbon tetrachloride will dissolve about 2.5 ml *i. e.* the total expansion is only 0.0054 ml per ml carbon tetrachloride. This negligible correction has been disregarded in the calculation of the experiments. In the other solvents used the involved error is still smaller.

For the solubility in water the experimental value was $\alpha = 0.754$ at 25° C. In the 0.15 per cent aerosol solution the values at 25° C were $\alpha = 0.750$ ($p_{CO_2} = 793.4$ mm) and $\alpha = 0.751$ ($p_{CO_2} = 725.2$ mm) *i. e.* 0.4 per cent less than in pure water. The relative surface tension of the aerosol solution was measured to be

Table 1. Solubilities of carbon dioxide expressed in Bunsen absorption coefficent (α). Experimental values at t° C.

n-C_7F_{16}	t			25.1	25.1			
	$p^{a)}$			669.3	686.4			
	α			2.09	2.09			
n-C_7H_{16}	t		20.5	25.1	25.1			34.5
	p		718.6	712.4	710.3			727.7
	α		1.98	1.84	1.85			1.62
cyclo-C_6H_{12}	t			25.0	25.0			
	p			700.3	814.1			
	α			1.57	1.59			
CCl_4	t			25.0	25.1			
	p			613.5	652.1			
	α			2.47	2.46			
C_6H_6	t	20.4	20.5	25.0			29.7	34.2
	p	714.2	556.6	656.1			663.5	609.4
	α	2.65	2.62	2.43			2.33	2.17
CS_2	t			24.9	25.2	25.3		
	p			433.0	394.8	479.2		
	α			1.21	1.21	1.22		

a) p is the partial pressure of carbon dioxide in mm Hg.

Table 2. Solubility (α) of carbon dioxide at 25° C. Comparison with previous measurements.

	Water	Carbon tetrachloride	Benzene	Carbon disulphide
Just 1901 [9]	0.7564	2.102	2.222	0.797
Geffcken 1904 [10]	0.759			
Findlay and Shen 1912 [6]	0.756			
Kunerth 1922 [11]	0.749			
Gatterer 1926 [12]	0.757			
Morgan and Pyne 1930 [13]	0.7572			
Horiuti 1931 [8]		2.444		
Orcutt and Seevers 1936 [14]	0.753			
Kiss, Lajtai and Thury 1937 [15]	0.7504			
Present investigation	0.754	2.47	2.43	1.21

0.431 in a stalagmometer according to Traube, the number of drops of water being 62 and for the aerosol solution 144.

It appears from Table 2, which includes solubilities found by other investigators that the present results for the solubility in carbon tetrachloride, benzene and carbon disulphide are higher than the results stated by Just. In carbon tetrachloride the present value differs only 1.5 per cent from the value found by Horiuti.

CORRELATION WITH THEORY

It was desired to investigate whether the solubility of carbon dioxide in non polar solvents can be represented by the equation

$$\log x_2^i = \log \Phi_2 + 0.4343\,(1 - \frac{V_2}{V_1})\,\Phi_1 + \frac{0.4343\,V_2\,\Phi_1^2}{RT}(\delta_1 - \delta_2)^2 \qquad \text{(I)}$$

where x_2^i denotes the 'ideal' solubility expressed in mole fraction, Φ volume fraction, δ solubility parameter, V molal volume, R the gas constant and T absolute temperature. Subscript 1 refers to the solvent and subscript 2 to carbon dioxide. With regard to the derivation of equation (I) reference should be made to Hildebrand and Scott [16]. The introduction of the approximation $\Phi_1 = 1$ just evolves a slight error since Φ_2 in all the solvents used is less than 0.0058. If further $\Phi_2 = \frac{V_2x_2}{V_2x_2 + V_1x_1}$ is substituted, equation (I) can be written

$$-\log x_2 = -\log x_2^i + \log \frac{V_2}{V_1} + 0.4343\,(1 - \frac{V_2}{V_1}) + \frac{0.4343\,V_2}{RT}(\delta_1 - \delta_2)^2 \qquad \text{(II)}$$

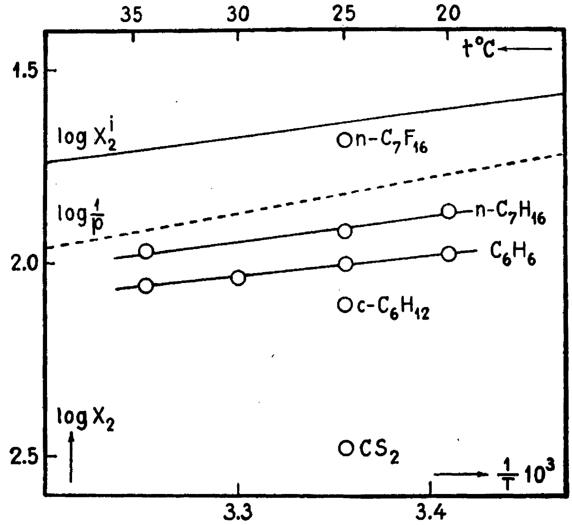

Fig. 1. The solubility of carbon dioxide
———— *log x_2^i ideal solubility of carbon dioxide*
– – – – – – – *ideal solubility disregarding deviations from perfect gas laws*
○ *experimental values of the solubility*

where x_2 is the solubility expressed in mole fraction. If we introduce the approximation $V_1 = V_2$ equation (II) is simplified into

$$-\log x_2 = -\log x_2^i + \frac{0.4343\ V_2}{RT}(\delta_1 - \delta_2)^2 \qquad \text{(III)}$$

The ideal solubility is calculated from

$$x_2^i = f_2/f_2^0 \qquad \text{(IV)}$$

where f_2 denotes the fugacity of carbon dioxide at one atmosphere and f_2^0 the fugacity at the saturation pressure, both calculated at the same temperature. The values of the fugacities are taken from Deming and Deming [17].

At 25° C we calculate $x_2^i = 0.9947/43.3 = 0.0230$. The curve for the ideal solubility is drawn in Fig. 1, using the reciprocal absolute temperature as abscisse and the logarithm of the ideal solubility as ordinate. For comparison the dotted curve shows values of $1/p_2^0$, which do not allow for the deviations of carbon dioxide from perfect gas laws. Also there are in Fig. 1 plotted experimental values for the solubilities converted to mole fraction by

$$x_2 = \frac{\alpha/22\,250}{\alpha/22\,250 + d/M}$$

where 22 250 is the molal volume in ml of carbon dioxide at 0° and 1 atm., and d and M is the density and molecular weight, respectively, of the solvent.

Table 3. Calculation of the solubility parameter (δ_2) for carbon dioxide at different temperatures.

$t°$	ΔH cal/g	ΔH cal/mole	p atm.	Specific vol. in ml liq.	Specific vol. in ml gas	Molal volume liq.	Molal volume gas	δ_2
−50	80.6	3 540	6.75	0.867	55.4	38.2	2 440	9.10
−40	76.6	3 370	9.93	0.897	38.2	39.5	1 680	8.68
−30	72.4	3 180	14.1	0.931	27.0	41.0	1 190	8.25
−20	67.8	2 980	19.4	0.971	19.5	42.7	859	7.80
−10	62.5	2 750	26.1	1.019	14.2	44.8	625	7.30
0	56.1	2 470	34.4	1.081	10.4	47.6	457	6.68
10	48.1	2 120	44.4	1.166	7.52	51.3	332	5.95
20	37.1	1 630	56.5	1.298	5.26	57.1	232	4.94
25	28.5	1 255	63.5	1.417	4.17	62.3	184	4.13
30	15.1	665	71.2	1.677	2.99	73.8	132	2.76
31	0	0	73.0	2.18	2.18	96.	96	

The value of V_2 for carbon dioxide (47.7 ml) is calculated as the average value of the partial molal volumes in carbon tetrachloride and benzene on the basis of Horiuti's experiments [8]; these values are only to a slight extent dependent on the solvent.

The solubility parameters (δ_1) of the solvents, defined as the square roots of their energy of vaporization per ml, are taken from Hildebrand and Scott [16]. For carbon dioxide δ_2 has been calculated from

$$\delta_2 = \sqrt{\frac{\Delta H - p\Delta V}{V_2}} \tag{V}$$

Table 4. Solubility of carbon dioxide in non polar solvents at 25° C. Comparison of experimental and calculated values. $x_2^i = 0.0230$; $V_2 = 47.7$ ml; $\delta_2 = 5.1$

				$-\log x_2$				
	V_1	δ_1	$x_2 \cdot 10^4$ exp.	exp.	calc. eq. II	ΔII	calc. eq. III	ΔIII
n-C_7F_{16}	227	5.85	209	1.68	1.32	−0.36	1.66	−0.02
n-C_7H_{16}	147	8.1	121	1.92	1.76	−0.16	1.83	−0.09
cyclo-C_6H_{12}	109	8.2	77.2	2.11	1.86	−0.25	1.97	−0.13
CCl_4	97.1	8.6	107	1.97	1.98	+0.01	2.07	+0.10
C_6H_6	89.3	9.15	96.6	2.02	2.14	+0.12	2.21	+0.19
CS_2	60.6	10.0	32.9	2.48	2.47	−0.01	2.48	+0.00

where ΔH is the molal heat of vaporization and ΔV the difference between the molal volume of carbon dioxide in the gaseous and the liquid state (V_2) at the pressure p. Requisite data (Quinn and Jones[18]) are given in Table 3. It turned out that it was not possible to represent the experimental values using equations (II) or (III) and the value $\delta_2 = 4.1$ at 25° C. The proper value of δ_2 to use for carbon dioxide was then determined from the solubility data themselves. The accuracy with which equations (II) and (III) together with the constant thus determined ($\delta_2 = 5.1$) represent the experimental results, will appear from Table 4. It can be seen that equation (III) expresses the experimental data somewhat better than equation (II).

It is interesting to notice that the experimental value for the solubility of carbon dioxide in benzene is 40—50 per cent higher than calculated. Possibly this higher solubility can be explained by assuming that carbon dioxide and the electron donor benzene form a weak compound. Recently Benesi and Hildebrand[19] proved by spectrophotometric measurements that there is a complex formation between iodine and benzene, and showed how this can explain the abnormal high solubility of iodine in benzene.

Correlation between the solubility and the surface tension of the solvents. The Ostwald's solubility coefficient, λ, can be calculated according to Uhlig[20] from

$$\ln\lambda = \frac{-\,4\pi r^2\sigma + E}{kT} \tag{VI}$$

where r denotes the radius of the dissolved gas molecule, σ the surface tension of the solvent, k Boltzmann's constant and T absolute temperature. E is an energy quantity originating in the attraction between the dissolved gas molecules and the molecules of the solvent. The value of E can be evaluated from the solubility measurements. It should be emphasized that equation (VI) is only valid for the solubility in pure solvents and not for the solubility in mixed solvents or *e. g.* for the solubility in a solution of aerosol in water. By dissolving even minor amounts of aerosol in water we get a considerable change of the surface tension, which for the 0.15 per cent solution used had a value less than half of the value for pure water. In spite of this the solubility of carbon dioxide showed the same value in both solvents. In such a diluted solution E may be assumed to have the same value as in pure water, and it is obvious that in this case equation (VI) will fail. For a pure solvent the surface tension is a function of the forces of attraction between the molecules of the solvent. Thus it is possible to calculate an approximate solubility parameter of a pure solvent from its surface tension, see Hildebrand and Scott[16 p. 431].

SUMMARY

1. Following values for the solubility of carbon dioxide, expressed as Bunsen coefficient, have been determined. In perfluoro-*n*-heptane 2.09 (25°), *n*-heptane 1.98 (20.5°), 1.85 (25°), 1.62 (34.5°), *cyclo*-hexane 1.58 (25°), carbon tetrachloride 2.47 (25°), benzene 2.63 (20.5°), 2.43 (25°), 2.33 (29.7°), 2.17 (34.2°) and in carbon disulphide 1.21 (25°).

2. The solubility equation for regular solutions, with an empirical adjustment of the solubility parameter of carbon dioxide, yields calculated values in reasonably good agreement with the experimental ones.

3. It is shown by experiment that the solubility of carbon dioxide in water and in a solution of 0.15 per cent aerosol in water have the same value to within the accuracy of the experimental determination. This gives an example in which the solubility is independent of the surface tension of the solvent.

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