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SOLUBILITY OF OZONE IN SOME FLUOROCARBON SOLVENTS

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SUMMARY

The solubilities of ozone 0-6 Wt% in air or oxygen, in 14 fluorocarbon solvents have been determined at ambient temperature. Solubilities ranged from 50 to 700 ppm (wt) for a gas phase O_3 concentration of 6 Wt%. Compounds with O_3 solubilities <130 ppm (wt), exhibited approximate Henry's Law behavior, whereas those compounds with O_3 solubilities >200 ppm (wt) showed apparent marked Henry's Law deviations.

INTRODUCTION

The solubility of oxygen and carbon dioxide in fluorocarbons has been well documented, [1,2,3] and has led to their use as blood substitutes. The high solubilities of these and other gases in fluorocarbons has been related qualitatively to their intermolecular empty volumes [4]. The latter has been postulated to exist to justify the observation that many fluorocarbons have high compressibility factors. Recently, in this laboratory, a need arose for a liquid with a high ozone solubility, that would be inert to the ozone chemically, and that would not be photolysed to any marked extent by 254 mm Hg arc irradiation. Both from chemical and photochemical [5] considerations, fluorocarbons appeared to be likely candidates. The solubilities of ozone in 14 fluorocarbons were determined with the results reported below.

EXPERIMENTAL

Ozone was generated in a Welsbach Ozonator Model T-23 using dry air or oxygen. Flow rates through the generator ranged from 250-1,000 ml/min. By

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varying the applied voltage, maximum ozone concentrations up to ≈3 and 6 Wt% were possible with air and oxygen, respectively. Except in some preliminary experiments, to determine if the gas flow rate had any effect on the measured ozone solubilities, all reported data are for ozone carrier gas flow rates of 600 ml/min through the fluorocarbon to be saturated. All surfaces in contact with ozone were fabricated from 316 stainless steel, Teflon or pyrex glass. The fluorocarbons, usually between 30-80 ml were held in a pyrex glass tube 22 mm ID and 400 mm, long (contact tube). The tube was terminated by a stopcock at it lower end. The ozone carrier gas stream was bubbled into the liquid through a pyrex frit for a period of 5-10 minutes. The surface temperature of the contact tube was monitored during the saturation period. With the more volatile solvents, the gas flow through the solvent resulted in cooling. In reporting the data, the lowest surface temperature attained during the experiment has been recorded. Immediately after terminating the ozone gas flow, the fluorocarbon solution was transferred from the contact tube into a weighed potassium iodide solution. To avoid loss of ozone during this transfer, the saturated ozone solution exited the contact tube via a stopcock through an 8 mm OD glass tube, the end of which was below the surface of a potassium iodide solution. The combined weight of the KI + ozone-fluorocarbon solution was obtained to determine the mass of fluorocarbon solvent transferred. After vigorously shaking the solutions, the KI solution was acidified (H_2SO_4) and titrated with 0.01N sodium thiosulfate using a starch indicator. Some fluorocarbon solvents, usually those of high ozone solubility, dissolved some iodine released in the KI/ozone reaction. Gently warming the solution with vigorous agitation was necessary to reach the final end point of the titration.

MATERIALS

The fluorocarbon solvents used in this study are listed in Table 1. With the exception of the two Krytok liquids (DuPont), all solvents were obtained from SCM Specialty Chemicals with claimed purities of >97%. Except for Freon 113, only limited quantities of the solvents were available. For these materials, the tested solvent was recovered from the titration flask and the moisture removed with 'DriRite'. The solvent was then reused for ozone solubility determinations. Apart from the latter drying procedure, all solvents were used as received.

TABLE 1

Fluorocarbon solvents used for ozone solubility studies

Compound No.	Name	Formula	MW	Boiling Point, °C	Density, g/cc (25°C)
1	1,1,2-trichlorotrifluoroethane (Freon 113)	$C_2F_3Cl_3$	187.5	48	1.553
2	Perfluoro-2-butyltetrahydrofuran	$C_5F_{16}O$	416.6	99-107	1.79
3	Perfluorohexane (85% n-isomer)	C_6F_{14}	338	59-60	1.66
4	Perfluoro-1-methyldecalin	$C_{11}F_{20}$	493.1	159-160	1.93
5	Perfluorodecalin	$C_{10}F_{18}$	462.1	141-142	1.93
6	1,2-dichlorohexafluorocyclobutane	$C_4Cl_2F_6$	233	59-60	1.50
7	Chloropentafluorobenzene	C_6ClF_5	202.5	117	1.63
8	Perfluoromethylcyclohexane	C_7F_{14}	350	76	1.76
9	Krytok 143 AZ	$(C_5F_{12}O)n$	≈1700	>285	1.84
10	Krytok K10-decamer	$(C_5F_{12}O)n$	≈1700	>285	1.84
11	1,2-dibromohexafluoropropane	$CBrF_2CBrFCF_3$	309.8	72.8	2.13
12	1,1,1-trichloroethane	CCl_3CH_3	187.5	45	1.33
13	1,1,1,3-tetrachlorotetrafluoropropane	$CCl_3CF_2CClF_2$	254	114	1.69
14	1,1,2,2-tetrachlorotetrafluorocyclobutane	$C_4F_4Cl_4$	256	--*	--

*Solid compound, Mp = 42.3°C

RESULTS AND DISCUSSION

Since Freon 113 was readily available, a relatively large number of experiments was made with this material to determine the required operating conditions for the solubility study. On the basis of data shown in Table 2 (presented graphically in Fig. 1), it was determined that a contact time of two minutes was sufficient to obtain equilibrium solubility values. Contact times of 5 to 10 minutes were most often used to ensure establishment of gas-liquid equilibrium. While larger samples would have produced more accurate data, samples as small as 20 g gave consistent results. No difference was noted with air or oxygen as the carrier gas. The experimental procedures are believed to be accurate to within ±7%; any systematic errors such as ozone loss during fluid transfer, ozone self-reaction, or iodine solubility in the solvent would result in the quoted solubility data being too low.

The solubility of ozone in 1,1,2,2-tetrachlorotetrafluorocyclobutane had to be determined in a slightly different way than that of the other fluorocarbons since this compound was a solid at ambient temperature. In order to perform solubility tests, the material was dissolved in Freon 113. Solutions containing 52, 60, and 65 Wt% of the cyclo-compound in Freon 113 were subjected to limited ozone solubility testing.

Data of the type shown in Table 2 and Fig. 1 were generated for each of the fluorocarbons, though the number of experimental determinations for each material was not so extensive as with Freon 113. In plotting solubility curves from the experimental data points, a linear relationship between the gas phase ozone concentration, and the dissolved mass ozone concentration was assumed. This approach was consistent with ozone solubility following Henry's Law behavior. The equation, $Y = A + BX$, rather than $Y = BX$, was used to fit the data, since it was clear that for many of the solvents the data did not extrapolate to the $Y = X = 0$ point. Y is the solution ozone solubility in ppm (wt), A and B are constants, and X is the gas phase O_3 concentration in Wt%. Data thus derived are presented in Table 3 for the materials studied.

For the compounds listed in Table 3, the solubility data appear to fall into two groups. Those materials, compounds #5-14 (Table 3), whose ozone solubility followed an approximate Henry's Law relationship over the 0-6

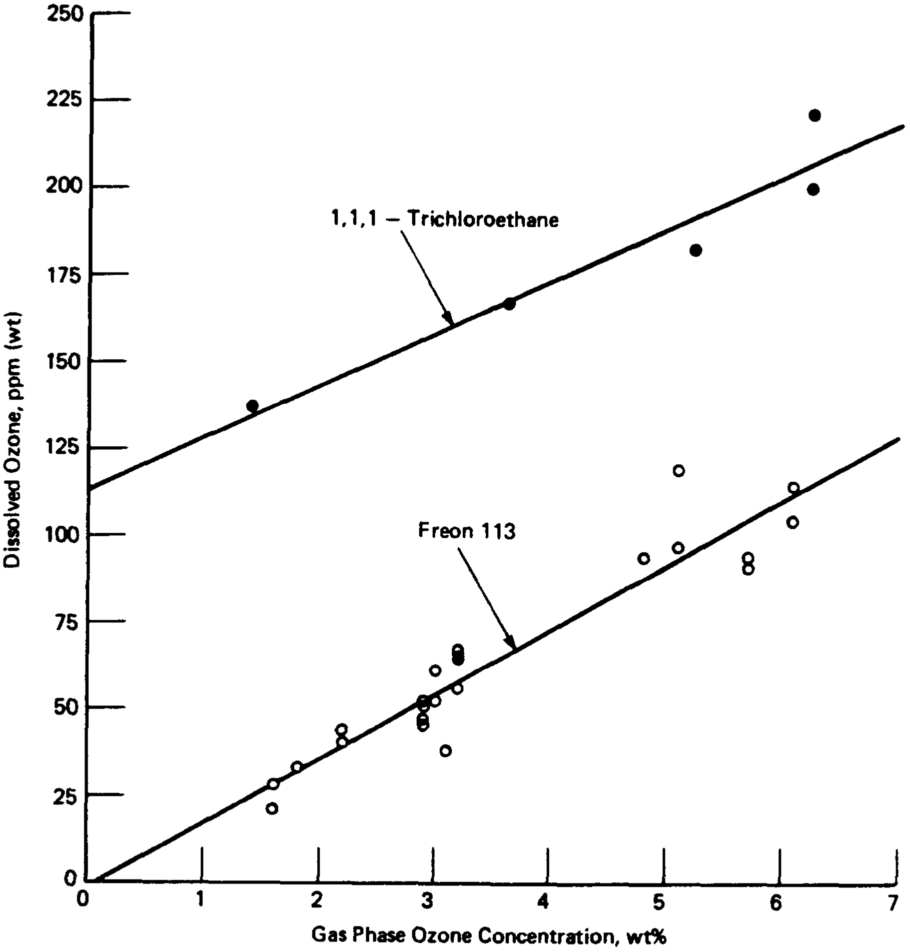

Fig. 1. Plots of the experimental data for the solubilities of ozone in Freon 113 and 1,1,1-trichloroethane.

Wt% gas phase ozone concentration range investigated. In most cases, the extrapolated curves did not intersect the X = Y = 0 point as required by Henry's Law. However, deviations from the X = Y = 0 point can probably be attributed largely to experimental errors in determining the individual data points and to the limited number of determinations made. A second group of solvents, compounds #1-4 (Table 3), exhibited ozone solubilities

TABLE 2

Ozone solubility data for Freon 113

Volume Tested, ml	Test Time, min	Test Temp., °C	Ozone Carrier	Ozone Conc., Wt%	Sample Size, g	Ozone Dissolved, mg	Wt, ppm Dissolved	Vol. O_3 ml* per 100 ml of Solvent
80	5	13	oxygen	5.7	75.3	7.1	94	6.8
80	10	11	oxygen	5.7	67.0	6.1	91	6.6
80	10	11	oxygen	3.1	60.5	2.3	38	2.7
80**	5	10	oxygen	1.8	64.8	2.2	33	2.5
80**	10	7	oxygen	4.8	62.8	5.9	94	6.8
90	10	10	oxygen	2.9	50.0	2.3	47	3.4
90	10	10	oxygen	2.9	47.3	2.1	45	3.3
80	10	11	air	1.8	58.5	1.9	33	2.5
80	5	12	air	3.2	68.3	4.4	65	4.7
90	10	12	air	3.2	67.2	4.5	67	4.8
90	10	12	air	3.2	50.1	3.2	64	4.6
60	5	12	air	1.6	60.8	1.7	28	2.0
40	1	16	air	1.6	52.1	1.1	21	1.5
40	2	13	air	1.6	59.5	1.7	28	2.0
40	2	16	air	2.2	50.0	2.0	40	2.9
40	5	10	air	2.2	45.5	2.0	44	3.2
50	2	16	air	2.9	57.5	2.9	50	3.6
40	5	11	air	2.9	55.5	2.9	52	3.8
40	2	16	air	3.2	46.3	2.6	56	4.0

40	5	12	air	3.2	59.2	3.9	65	4.7
40	2	12	oxygen	3.0	50.7	3.1	61	4.4
40	2	16	oxygen	3.0	58.2	3.0	52	3.8
40	2	17	oxygen	5.1	56.4	5.5	97	7.0
40	5	11	oxygen	5.1	50.1	6.0	119	8.6
40	5	12	oxygen	6.1	53.0	5.6	105	7.6
40	2	16	oxygen	6.1	53.2	6.1	115	8.3

*Volumes of ozone correspond to the gas at one atmosphere pressure and 273K

**Flow rate: 1 1/min; all other tests @ 0.6 1/min

TABLE 3

Solubility parameters of O_3 in some fluorocarbon solvents presented in order of effectiveness on a weight basis

	Compound	Coefficients A	Coefficients B	Correlation Coefficient R^2	Gas Phase $[O_3]$[b] Range %	No. of Expt. Points	O_3 Wt ppm[c] Dissolved	Volume O_3 (ml)[c,d] per 100 ml of Solvent
1	$C_2F_3Cl_3$ + 60 Wt% $C_4F_4Cl_4$	a	a	a	a	3	770	57
2	$C_4Cl_2F_6$	158.0	47.6	0.716	0.7-6	7	430	30
3	CCl_3CH_3	110.9	17.4	0.923	1.5-6	5	215	13.3
4	C_6ClF_5	125.5	12.4	0.821	1.3-6	7	200	15.2
5	$CBrF_2CBrFCF_3$	0.4	20.6	0.984	0-6	7	130	12.9
6	Freon 113	-1.55	18.66	0.909	0-6	28	120	8.6
7	$CCl_3CF_2CClF_2$	-2.1	20.4	0.997	0-6	5	120	9.5
8	C_6F_{12}	-16.6	19.8	0.952	0-6	10	100	7.8
9	$C_5F_{16}O$	-10.1	16.9	0.962	0-6	7	90	7.5
10	C_7F_{14}	-8.1	16.8	0.988	0-6	7	90	7.4
11	$C_{11}F_{20}$	-6.9	12.6	0.975	0-6	9	70	6.3
12	$C_{10}F_{18}$	-8.5	13.0	0.975	0-6	6	70	6.3
13	$(C_5\text{-}F_{12}O)n$	2.7	9.6	0.996	0-6	3	60	5.2
14	$(C_5\text{-}F_{12}O)n$	4.4	7.4	0.983	0-6	6	50	4.3

[a] Limited data - not determined

[b] Range of O_3 concentration in liquid phase over which solubility appeared to be linear

[c] This solubility corresponds to 6 wt% O_3 in the gas phase

[d] Volume O_3 calculated at NTP

that were linear over the range in which measurements were made. Extrapolation of the derived linear solubility curve to X = 0 clearly did not result in a Y value close to zero. An example of this behavior is shown in Fig. 1 for 1,1,1-trichloroethane.

For those compounds #5-14 (Table 3) in which Henry's Law was approximately followed, the ozone solubilities fall in the 50-130 ppm range, whilst for those materials apparently deviating from Henry's Law, ozone solubilities were in the 200-770 ppm range. It is difficult to account for the differing ozone solubilities within the two groups of compounds. It is possible those solvents with high ozone solubility may have reacted with ozone to form stable O_3 adducts which on addition of KI solution released iodine that was subsequently titrated and quantified as free O_3. Alternatively, there may have been impurities in the solvents that on treatment with ozone may have released species capable of oxidizing KI. This latter possibility would require a rather high level of such impurities since repeated use of the same solvent did not have any noticeable effect on the results.

As noted earlier, oxygen has a marked solubility in some fluorocarbon solvents. The highest reported [1] solubility of O_2 in a fluorocarbon solvent is 57.2 ml of O_2/100 ml of solution at 25°C for pure oxygen in the gas phase at 1 atmosphere pressure. Considering that the solubility values reported for O_3 in Table 3 correspond to only 6 Wt% O_2 in the gas phase, the solubility of ozone in some of the solvents tested is impressive. Indeed, those fluorocarbon solutions with higher ozone contents were pale blue in color, an observation consistent with the known deep blue coloration of pure ozone gas. Limited tests on the stability of a solution of O_3, 260 ppm (wt), dissolved in 1,2-dichlorohexafluorocyclobutane, showed no detectable O_3 loss over a period of 30 minutes.

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