Physical Properties and Gas Solubilities in Selected Fluorinated Ethers

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The density and viscosity of three fluorinated ethers were measured over a range of temperatures, and the solubilities of O_2, N_2, and CO_2 in these compounds were also measured. The experimental data agreed reasonably well with the predictions of perturbation theory.

Fluorocarbons, in general, possess unusual properties, and this seems particularly true of some of the fluorinated ethers which exhibit surprisingly large gas solubilities. Several of these have attracted considerable interest in medical research as potential oxygen carriers in liquid breathing (*6*), in cardiopulmonary bypass machines (*4*), and as blood substitutes (*9*). It is, therefore, of both practical and theoretical interest to determine such physical properties as density, viscosity, and the solubility of gases in selected fluorinated ethers. Three of these, Caroxin-D (perfluoro-1,4 diisopropoxy butane) (Allied Chemical Corp., Morristown, N.J.), Caroxin-F (perfluoro-1-isopropoxy hexane) (Allied Chemical Corp., Morristown, N.J.), and FC-80 (perfluorobutyl perfluorotetrahydrofuran) (3M Co., St. Paul, Minn.), have been studied in this work.

Experimental

Materials. Minimum purities of O_2, N_2, and CO_2 were 99.6%. Caroxin-D and Caroxin-F were of greater than 99.9% purity as supplied. FC-80 contains several isomers as supplied (*2*).

Procedure. The experimental method of Shoor et al. (*8*) was used in solubility measurements. Saturation of the liquid was accomplished by bubbling the gas through the liquid in a saturator. The gas was dispersed through the liquid by a fritted glass disk at a rate of about 40 ml/min. Samples were withdrawn with a Hamilton Microliter syringe at 15-min intervals (after an initial equilibration period of 30 min) and analyzed chromatographically. The syringe was flushed several times before sampling. Fifteen μl of the gas-saturated liquid were injected directly into the injection port of a Perkin-Elmer Model 900 gas chromatograph with a thermal conductivity detector.

The column used was a $\frac{1}{8}$-in. × 12-ft Porapak Q column, which was kept at room temperature. Calibration of the chromatograph was made by injecting accurately known volumes of pure, dry gas at room temperature and atmospheric pressure. The time required to saturate the solution was determined by withdrawing samples periodically and considering the solution saturated when the dissolved gas concentration remained constant for an hour. The solubility reported is the mean value of three consecutive samples which agreed within the limits of experimental errors.

The saturator was maintained at the desired temperature by immersing it in a constant temperature bath maintained to 0.05°C. Thermometers were calibrated against NBS-certified thermometers.

For density and viscosity measurements, a pycnometer and a Cannon-Fenske viscometer were used. Each measurement was taken three times.

Results

The density and viscosity of Caroxin-D, Caroxin-F, and FC-80 are tabulated in Table I. This table also lists commercial data for comparison (*5*). Solubility data at 1-atm partial pressure are tabulated in Table II. Our experiments with Caroxin-F at 25°C and different partial pressures of CO_2 and O_2 show that Henry's Law is obeyed. It is assumed, therefore, that this is true for the other two compounds. Oxygen, nitrogen and carbon dioxide were all most soluble in Caroxin-F and least soluble in FC-80.

For interpolation purposes, these results can be expressed in the form

$$\ln S = \frac{A_1}{T} + A_2 \qquad (1)$$

when S is the solubility in mole fraction, T is the absolute temperature K, and A_1 and A_2 are constants given in Table II. Equation 1 should not be used for extrapolation.

Table I. Densities and Viscosities of Fluorocarbons

Temp, °C	Caroxin-D	Caroxin-F	FC-80
	Densities, g/cc		
25	1.7465 (1.75)[a]	1.7449 (1.748)	1.7657
30	1.7337 (1.74)	1.7326 (1.736)	1.7524
35	1.7205 (1.727)	1.7196 (1.722)	1.7395
40	1.7078 (1.713)	1.7069 (1.71)	1.7264
50	1.6818 (1.688)	1.6813 (1.685)	1.7003
	Viscosities, cP		
25	2.0579 (2.12)	1.5405 (1.6)	1.3953
30	1.8676 (1.92)	1.4118 (1.45)	1.2702
35	1.6961 (1.73)	1.2852 (1.33)	1.1595
40	1.6045 (1.58)	1.1790 (1.22)	1.0659

[a] Ref. 5.

Table II. Solubility of Gases in Fluorocarbons
Solubility, mole fraction $\times 10^3$

Fluorocarbon	Gas	25°C	30°C	37°C	40°C	50°C	A_1[a]	A_2[a]
Caroxin-D	O_2	6.50	6.40	6.30	6.28	6.20	101.870	−5.3951
	N_2	5.00	4.94	4.89	4.83	4.75	105.059	−5.666
	CO_2	24.8	23.8	22.7	22.4	20.6	181.689	−4.364
Caroxin-F	O_2	6.60	6.57	6.48	6.47	6.30	88.573	−5.328
	N_2	5.10	5.05	4.97	4.92	4.80	121.429	−5.702
	CO_2	25.0	24.3	23.2	22.8	21.4	314.418	−4.790
FC-80	O_2	5.60	5.58	5.50	5.50	5.40	72.351	−5.436
	N_2	4.30	4.18	4.03	4.00	3.80	254.264	−6.338
	CO_2	22.3	21.0	18.6	17.72	15.50	761.299	−6.461

[a] Constants for Equation 1.

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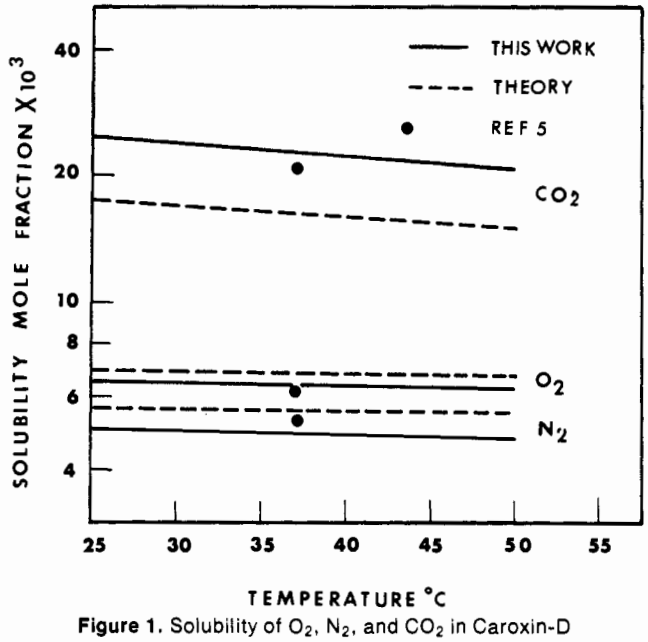

Figure 1. Solubility of O_2, N_2, and CO_2 in Caroxin-D

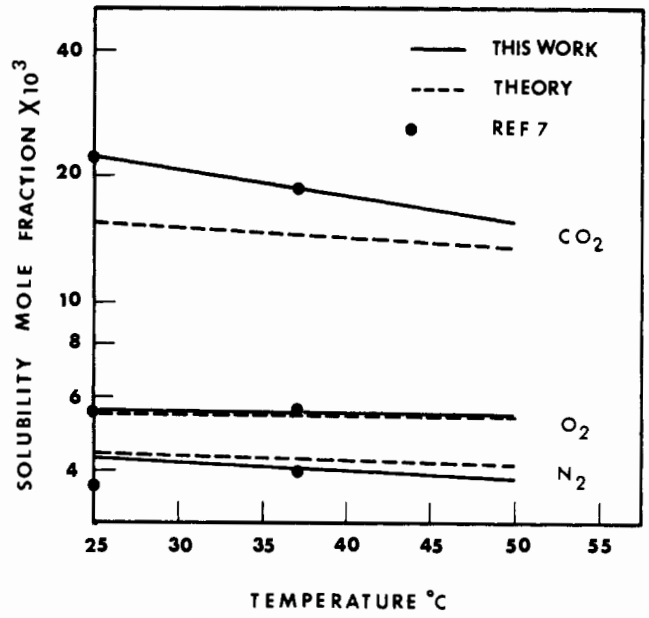

Figure 3. Solubility of O_2, N_2, and CO_2 in FC-80

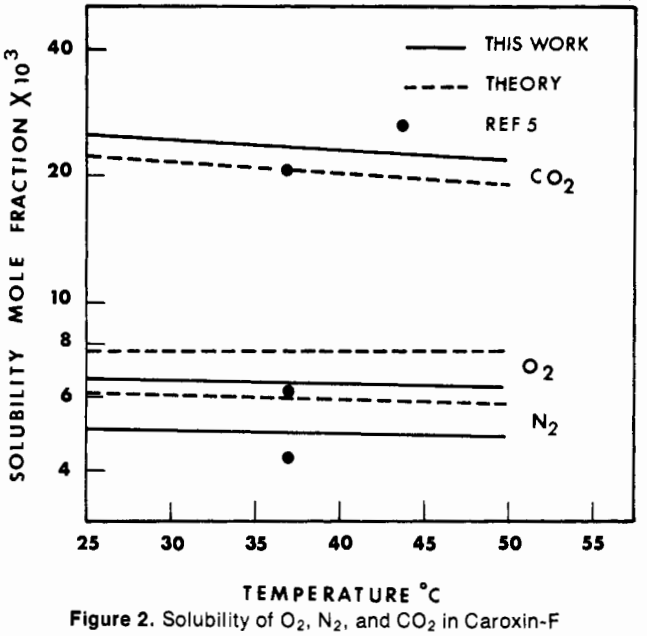

Figure 2. Solubility of O_2, N_2, and CO_2 in Caroxin-F

Comparisons with Theory

Tiepel and Gubbins (*11*) proposed a treatment of gas solubility based on perturbation theory. For calculations of solubility, liquid densities and molecular potential parameters are needed. The potential parameters for gases are those given by Hirschfelder et al. (*1*) derived from second-virial coefficients. The corresponding values for fluorocarbons were calculated with the correlation of Tee et al. (*10*). Estimations of critical constants were made by use of known normal boiling points and group contributions (*3*).

The calculated results are plotted in Figures 1–3, together with the experimental data and some data from the literature (*5*, *7*). The agreement with data of the literature is, in general, within ±5%. The agreement between calculated and experimental results is good for O_2 and N_2 in fluorocarbons. The differences between these values for CO_2 are considerably higher. This may be due to high polarity of CO_2 gas and significant deviation from the spherical shape of the CO_2 molecules.

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