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Solute–Solvent Interactions in Perfluorocarbon Solutions of Oxygen. An NMR Study

M'Hamed Ali Hamza, Guy Serratrice, Marie-José Stébé, and Jean-Jacques Delpuech*

Contribution from the Laboratoire de Chimie Physique Organique, ERA CNRS 222, Université de Nancy I, C.O. 140, 54037 Nancy Cedex, France. *Received November 17, 1980*

Abstract: Fluorinated compounds, including alkanes, alkenes, aromatics, amines, and cyclic and heterocyclic fluorochemicals, are studied as solvents of oxygen, using for this purpose the paramagnetic relaxation induced by the presence of molecular oxygen onto the ^{13}C nuclei of neighboring solvent molecules in the solution. Relaxation data are expressed by the variation rates q_x of relaxation rates T_1^{-1} per mole fraction of dissolved oxygen. A general correlation is found between the solubility of oxygen (in mole fraction) and the relaxation coefficients q_x, the lower q_x values being associated to the higher solubilities. This was accounted for by the existence of large cavities in the liquid for the better solvents, which can thus accommodate small gaseous molecules more easily, while simultaneously the magnetic dipolar interaction between oxygen and solvent nuclei is decreased. The sequence found for compounds of decreasing solubility, aliphatic > cyclic > aromatic, can be rationalized on the basis of cavities of decreasing size from one class of solvents to the other. The order of solubility seems to depend mainly upon the shape of solvent molecules and not upon the details of molecular structure, thus discarding the alternative assumption of specific fluorine–oxygen forces and of a possible charge-transfer complex. The higher relaxation coefficients obtained for some typical analogous hydrocarbons can be rationalized by using the same concepts.

Compared to hydrocarbons, fluorocarbons have physical properties which seem to be exceptional in many respects.[1] It was indeed soon recognized that, apart from a superficial similarity arising from the carbon skeleton, the hydrocarbon and fluorocarbon molecules do not offer more analogies in their physical and chemical properties than those existing between hydrocarbons and the compounds deriving from any of the other elements of the periodic table. Compounds of hydrogen form in fact a class by themselves due to the very unusual properties of hydrogen nuclei. The difference between the physical properties of hydrogenated and fluorinated liquids is emphasized by the very nonideal behavior of mixtures of hydro- and fluorocarbons. This was traced to the existence of quite different intermolecular dispersion forces as a result of large differences in the ionization potentials of hydro- anf fluorocarbons. Another difference lies in the importance of the details of molecular structure in accounting for the properties of hydrocarbons, while they appear to be unimportant parameters in the fluorinated species. *Liquid fluorocarbons are therefore much more representative of nonpolar nonassociated solvents.*

These compounds are endowed with much higher viscosities, smaller liquid isothermal compressibilities, and lower boiling points and surface tensions[1-5] (Table I). An interesting peculiarity of these compounds is the higher solubility of gases (Table II). The study of this solubility is the general purpose of a research project planned in this laboratory a few years. Our attention was drawn first to solutions of molecular oxygen in fluorocarbons. Highly fluorinated liquids are known to dissolve significant quantities of molecular oxygen.[2-7] The molarity of these solutions is of the same order of magnitude as that of molecular oxygen in normal air. This property has suggested a probable utility of fluorinated solvents as *oxygen carriers* in artificial blood and liquid breathing.[8-10] For the sake of comparison, it should be noted that the solubility of oxygen in fluorocarbons is about three to ten times as large as that observed in the parent hydrocarbons or in water, respectively (Table II).

Table I. A Comparison of the Physical Properties of Some Hydrocarbons and Fluorocarbons

compd	mol wt[a]	$[S_0]$[b]	E[c]	η[d]	ρ[e]	γ[f]	β[g]
n-C_6H_{14}[h]	86.18	7.60	68.7	0.298	0.655	17.9	17.10[i]
n-C_6F_{14}[i]	338.04	4.94	58	0.66	1.672	12.0	27.66
n-C_7H_{16}[h]	100.20	6.78	98.4	0.397	0.679	19.8	14.40[i]
n-C_7F_{16}[i]	388.05	4.43	83	0.90	1.719	12.7	23.31
C_6H_6[h]	78.11	11.20	80.1	0.603	0.874	28.2	9.70[j]
C_6F_6[h]	186.06	8.65	80.3	0.90	1.607	22.6	

[a] Molecular weight. [b] Molarity of the pure compound at 25 °C. [c] Normal boiling point (°C). [d] Viscosity (in cP at 25 °C). [e] Density at 25 °C. [f] Surface tension (in dyn cm^{-1} at 25 °C). [g] Liquid isothermal coefficient (in N^{-1} m^2 × 10^{10} at 30 °C and 1 atm). [h] J. A. Riddick and W. B. Bunger, "Techniques of Chemistry", Vol. II, "Organic Solvents", 3rd ed, Wiley-Interscience, New York, 1970. [i] Reference 1. [j] G. A. Holder and E. Walley, *Trans. Faraday Soc.*, 58, 2095 (1965).

The paramagnetic shift and the paramagnetic relaxation induced by the presence of molecular oxygen within the fluorinated liquid is used in this work as a tool to obtain some information about solute–solvent interactions in these solutions. The method was first applied to hexafluorobenzene[11] and to partially or totally fluorinated alkanes or alkenes.[12] In this paper, other categories of fluorinated molecules are investigated: substituted fluoroaromatics, perfluorocyclohexene, perfluorotributylamine, and two heterocyclic compounds (perfluoro-N-methylpiperidine and -N-methylmorpholine). Collecting the whole set of our results for 18 solvents allows us to demonstrate a general correlation between the solubility of oxygen and the magnetic perturbation brought to the neighboring carbon nuclei of the solvent.

Experimental Section

Materials and Solutions. All the solvents which are investigated in this paper—compounds **2**, **3**, **4**, **5**, **7**, **8**, **9**, and **17** in Tables III–V—are PCR

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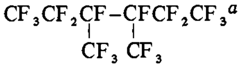
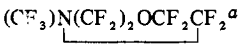
Table II. Solubilities of Gases in Blood, Water, and Some Typical Hydro- and Fluorochemicals[g]

solvent	solute				
	O_2	N_2	CO_2	Ar	H_2
blood	0.0082				
H_2O[b]	0.0013 0.23	0.00066 0.119	0.030 5.46	0.0014 0.25	0.00078 0.142
$n\text{-}C_7H_{16}$[c]	0.0160 21.7	0.0100 13.5	0.0890 120.2	0.0184 24.9	0.00508 6.86
$n\text{-}C_7F_{16}$[c]	0.0268 55.2	0.0140 38.8	0.101 208	0.0258 53.2	0.0068 14.0
$n\text{-}C_8F_{18}$[d]	0.0232 53.4				
 $CF_3CF_2CF(CF_3)-CF(CF_3)CF_2CF_3$[a]	0.0148 35.2				
C_6H_6[c]	0.010 8.1	0.0055 4.46	0.120 97.3	0.0108 8.81	0.0032 2.58
C_6F_6[c]	0.0217 24.2	0.0160 17.9	0.197 220	0.0214 23.9	
$c\text{-}C_6H_{11}CH_3$[c]	0.0124 16.0	0.0074 9.46	0.0731 92.8	0.143 18.4	
$c\text{-}C_6F_{11}CF_3$[c]	0.0233[e] 45.5	0.0166 32.7		0.0229 44.7	
$(C_4F_9)N$[c]	0.0167[a] 59.6	0.0098 34.9	0.0546 199	0.0172 61.0	
 $(C_4F_9)CF(CF_2)_3O$[f]	0.0213 46.2	0.0136 31.7	0.0785 179.7		
 $(CF_3)N(CF_2)_2OCF_2CF_2$[a]	0.0169 29.6				

[a] This work. [b] "Solutions and Solubilities", Part I, Mickael R. J. Dack, Ed.; "Techniques of chemistry", Vol. VIII, Arnold Weissberger, Ed. [c] Reference 4. [d] Reference 6. [e] Reference 1. [f] Reference 3. [g] 25 °C; 1 atm; in mol per dm^3 or in mole fraction × 10^4, first and second lines, respectively.

or Fluka products used without further purification. The other compounds, which are quoted from previous publications,[10,11] are also commercial products, except for compounds **11**, **13**, **14**, and **18**, which were generously supplied by the PCUK Company, compound **12**, prepared by Professors Cambon and Riess according to a described procedure,[13] and a sample of perfluoro-3,4-dimethylhexane (**19**), offered by the ICI Company. The ^{13}C NMR spectrum of these compounds gave no indication of impurities (compound **19** was found as a mixture of the two diastereoisomers). The techniques used to prepare the oxygen solutions are described in previous publications.[11,12] The concentration of oxygen in the solvent under pressure (up to 17 atm) is determined within the sealed NMR sample tube by an NMR procedure previously described.[14] This procedure uses the differences between externally referenced chemical shifts, $\delta_\perp$ and $\delta_\parallel$, produced by the difference in sample configuration in two spectrometers, one having a conventional electromagnet which applies the induction perpendicular to the sample axis ($\delta_\perp$) and the other a superconducting coil which applies the induction longitudinally, thus allowing the paramagnetic bulk susceptibility $\Delta\chi_v$ and the absolute paramagnetic shift $\Delta\sigma$ to be derived separately.

Carbon-13 Spin-Lattice Relaxation Times. Carbon-13 Fourier transform spectroscopy was performed with a Bruker HX-90 apparatus at 22.63 MHz (300 scans of 4K/8K points over a frequency range of 0.3–1.2 kHz), using broad band fluorine noise decoupling and a deuterium lock (external C_6D_6). Temperature was periodically checked with a thermometer immersed in the sample tube and was found to have a constant value of 28 ± 0.5 °C. Fluorine decoupling with the above equipment may be efficiently performed over a frequency range of about 1.2 kHz, which is smaller than the entire range of ^{19}F resonances. The entire $^{13}C\{^{19}F\}$ spectrum may however be reconstituted from several experiments in which the various fluorine nuclei are successively irradiated. The validity of the results thus obtained has been checked recently by using a Bruker WP-80 spectrometer equipped with a special high-power (50 W) decoupling unit which may cover the entire range of ^{19}F resonances (line width of the resulting ^{13}C singlets is 2–3 Hz). Proton noise decoupling was used to obtain the $^{13}C\{^1H\}$ spectra of the hydrocarbon samples which were studied for the sake of comparison. Triple irradiation was used to simultaneously decouple proton and fluorine nuclei in partially fluorinated hydrocarbons. The assignment of resonances to the corresponding nuclei of the investigated samples was discussed in previous publications.[11,12] Relaxation times of $^{13}C\{^{19}F\}$ or $^{13}C\{^1H\}$ or $^{13}C\{^1H,^{19}F\}$ nuclei at 22.6 MHz (Bruker HX-90) or 20.1 MHz (Bruker WP-80) are obtained from partially relaxed Fourier transform spectra, using the fast inversion recovery method.[15] Computations of T_1 values from the signal intensities were performed on a TI 980A minicomputer and were reproducible to ±5%. For each compound, the T_1 values of the different types of ^{13}C nuclei are determined in separate experiments. Measurements are carried out at 28 °C, using either the degassed solvent or four or five concentrations of dissolved oxygen.

Table III. Values of the Oxygen Solubility x_g, the ^{19}F Contact Shift $\Delta\sigma_X$ (in ppm, at low field), the Hyperfine Coupling Constant A_X (in MHz), and the Experimental ^{13}C Relaxation Coefficients q_c ($M^{-1}\ s^{-1}$) or q_x (s^{-1}) at 28 °C of Some Fluoroaromatics

no.	compd	10^4x_g	$\Delta\sigma_X$	A_X	q_c	q_x
1	C_6H_6	8.1			5.38	60.2
2	$1,4\text{-}C_6H_4F_2$	9.8			CH, 6.26 CF, 5.60	63.4 56.7
3	$1,3,5\text{-}C_6H_3F_3$	11.3			CH, 6.96 CF, 6.33	67.3 61.3
4	C_6F_5Cl	19.4	75.82 (para)	1.02	C2, 6.10	49.0
					C3, 6.19	49.7
					C4, 6.58	52.8
					C1, 5.89	47.3
5	$C_6F_5CF_3$	23.8	46.66 (CF_3)	0.63	C2, 5.04	35.5
					C3, 4.86	34.2
					C4, 5.24	36.9
					CF_3, 5.29	37.2
6	C_6F_6	25.4	55.53	0.74	4.71	40.7

Results

The solubilities of oxygen in the investigated solvents are reported in (Tables II to V). The mole fraction scale is particularly well fitted for comparisons of the solubilizing power since the obtained numbers $x_g \ll 1$ are quite close to the number of oxygen molecules dissolved in one mole of each solvent.

^{19}F $\Delta\sigma$ values have been used to estimate the paramagnetic shift $\Delta\sigma_M$ between molecules in the bulk solvent (the so called dia-

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Table IV. Values of the Oxygen Solubility x_g, the ^{19}F Constant Shift $\Delta\sigma_X$ (in ppm), the Hyperfine Coupling Constant A_X (in MHz), and the Experimental ^{13}C Relaxation Coefficients q_c (M^{-1} s^{-1}) or q_X (s^{-1}) at 28 °C of Some Aliphatic Fluorochemicals

no.	compd	10^4x_g	$\Delta\sigma_X$	A_X	q_c, q_X
10	$C_{10}H_{22}$	20.8			C1: 6.13, 31.4 C5: 4.76, 24.4
11	$C_8F_{17}CH{=}CH_2$	44.5			C1: 5.98, 22.2 C8: 4.60, 17.1 C10: 7.00, 26.0
12	$C_6F_{13}CH_2CH_2C_6F_{13}$	46.8			C1: 7.40, 18.9 C6: 5.40, 13.8 C7: 5.31, 13.5
13	$C_8F_{17}C_2H_5$	47.1	26.61 (CF$_3$)	0.358	C1: 5.85, 21.5 C8: 4.38, 16.1 C10: 7.49, 27.6
14	$C_8F_{17}C_8H_{17}$	52.2	19.15 (CF$_3$)	0.257	C1: 7.12, 18.9 C8: 5.50, 14.6 C16: 8.01, 21.2
15	n-C_7F_{16}	55.2	32.19 (CF$_3$)	0.433	C1: 5.78, 25.6 C4: 5.02, 22.2
16	n-C_6F_{14}	57.6	36.48 (CF$_3$)	0.490	C1: 4.75, 23.5 C3: 4.29, 21.2
17	$(n$-$C_4F_9)_3N$	59.6	20.02 (CF$_3$)	0.269	CF$_3$: 6.73, 18.8 α-CF$_2$: 4.48, 12.5
18	$C_6F_{13}CH{=}CHC_6F_{13}$	61.4	16.82 (CF$_3$)	0.226	C1: 6.29, 16.6 C5: 4.96, 13.1 C6: 6.44, 17.0 C7: 6.75, 17.8

Table V. Values of the Oxygen Solubility x_g, the ^{19}F Contact Shift $\Delta\sigma_X$ (in ppm), the Hyperfine Coupling Constant A_X (in MHz), and the Experimental ^{13}C Relaxation Coefficients q_c (M^{-1} s^{-1}) or q_X (s^{-1}) at 28 °C of Some Cyclic Fluorochemicals

no.	compd	10^4x_g	$\Delta\sigma_X$	A_X	q_c, q_X
7	c-C_6F_{10}	29.2	45.60 (CF)	0.613	CF: 4.31, 27.2 α-CF$_2$: 4.26, 26.6 β-CF$_2$: 4.11, 26.0
8	$(CF_3)\underline{N(CF_2)_4CF_2}$	32.5	37.77 (CF$_3$)	0.508	CF$_3$: 4.70, 24.6 α-CF$_2$: 4.67, 24.4 $\left.\begin{matrix}\beta\text{-CF}_2\\ \gamma\text{-CF}_2\end{matrix}\right\}$ 4.64, 24.3
9	$(CF_3)\underline{N(CF_2)_2OCF_2CF_2}$	29.6	41.16 (CF$_3$)	0.553	CF$_3$: 4.45, 25.4 N-CF$_2$: 4.12, 23.5 O-CF$_2$: 4.28, 24.4

magnetic site D) and those which are next neighbors to an oxygen molecule (the paramagnetic site M) according to the equations

$$\Delta\sigma = p_M\Delta\sigma_M = x_g\Delta\sigma_X$$

where

$$\Delta\sigma_X = n_M\Delta\sigma_M \text{ and } p_M = n_M C_g/[S_0] \simeq n_M x_g$$

n_M is the number of solvent molecules surrounding one oxygen molecule, p_M is the mole fraction of solvent molecules in the paramagnetic site, $[S_0]$ is the molarity of the pure solvent, and C_g is the molarity of oxygen in the solution. With the assumption that the paramagnetic shift arises from a Fermi contact interaction, we can derive a hyperfine constant A according to the classical formula[16]

$$\Delta\sigma_M = \frac{Ahg_e\beta_e}{g_N\beta_N}\,\frac{S(S+1)}{3kT}$$

where g_e and g_N are electronic and ^{19}F Landé factors; β_e and β_N are electronic and nuclear magnetons; h and k are Planck and Boltzmann constants; and S is the electronic spin number of the oxygen ($S = 1$). As n_M is an unknown constant, $\Delta\sigma_X$ (and therefore $A_X = n_M A$) rather than $\Delta\sigma_M$ (and A) values are taken into consideration, as if we assumed a 1:1 encounter complex (Tables III to V).

^{13}C relaxation times T_1 in oxygen solutions are not reported individually. Paramagnetic relaxation theories[17] predict a proportionality of the relaxation rate increase $1/T_{1r}$ (defined as the difference between the relaxation rates of the degassed and oxygenated solvent, $1/T_1^0$ and $1/T_1$, respectively) to the oxygen molarity C_g or mole fraction x_g

$$1/T_{1r} = 1/T_1 - 1/T_1^0 = q_x x_g = q_c C_g$$

with $q_x = q_c[S_0]$ (assuming fast exchange conditions). These predictions were confirmed in all cases, as shown by correlation coefficients ranging from 0.992 to 0.999 in least-squares analyses. The computed proportionality factors q_x and q_c, the so called relaxation coefficients, are reported in Tables III–V. Each of these values actually results from T_1 measurements over five solutions at least, and the set of these values summarizes all the information contained in these experiments.

Discussion

The Benzene–Oxygen and Perfluorobenzene–Oxygen Systems. Let us recall the conclusions, previously obtained for these systems,[11] which are necessary to interpret the whole set of our results. Nuclear relaxation arises from a dipolar interaction between the electronic spins of oxygen and the spins of the solvent nuclei modulated by the molecular motions. Relaxation rates in the C_6H_6/O_2 system may be accounted for by a continuous translational diffusion of oxygen in liquid benzene. This model may account for all the experimental facts: equal values of the longitudinal and transverse relaxation times which are dependent from the working frequency, and reasonable values derived for the electronic relaxation time of oxygen ($\tau_S = 0.9 \times 10^{-11}$ s) and

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the minimum distance of approach d_I of electronic and nuclear spins I (d_C = 3.08 Å and d_H = 2.93 Å). On the contrary, such a model of continuous diffusion led us to impossibilities if applied to the oxygen solutions in hexafluorobenzene. We had then to envisage a model in which the oxygen molecules have a short residence time $\tau_M \simeq 1$ ps in privileged positions of the C_6F_6 liquid lattice which they occupy successively by random jumps. Such a situation may be reached either by the existence of a short-lived complex or by the temporary encagement of one oxygen molecule in preexisting cavities or defects of the liquid lattice of the perfluorinated solvent. Although the first assumption cannot be absolutely ruled out presently, we have good reasons to take the cavity model into consideration only, as explained below. In this model, an assembly of n_M solvent molecules is assumed to enclose a vacancy of mean radius a in which an oxygen molecule stays during a mean residence time τ_M before migrating into another adjacent vacancy. Such a model leads to expressing the experimental slopes q_c or q_x as

$$q_c = \frac{n_M}{[S_0]}\frac{1}{T_{1M}} \text{ or } q_x = \frac{n_M}{T_{1M}}$$

T_{1M} is the relaxation time of the solvent nuclei around the paramagnetic oxygen molecule in the cavity and is given by Solomon–Bloembergen's equation[18]

$$1/T_{1M} = \frac{2 \times 10^{-14}}{15}\frac{\mu_M^2\gamma_I^2}{r_I^6}\tau_M$$

where $\mu_M = 2.80\ \mu_B$ is the electron spin moment of oxygen, γ_I the magnetogyric ratio of nucleus I, and r_I the distance between the centers of the oxygen molecules and the observed nucleus. Variable spatial positions are expected for ^{13}C and ^{19}F nuclei with respect to oxygen as a result of molecular motions inside the cavity and $\overline{1/r_I^6}$ actually represents a weighted mean $\langle 1/r_I^6 \rangle$ (=denoted as $\overline{1/r_I^6}$) which is very close to $1/a^6$ in the case of small tight-fitting cavities. Writing these equations successively for ^{13}C and ^{19}F nuclei of hexafluorobenzene allows us to derive a purely geometrical ratio $\overline{r_C/r_F} = 1.193$, which implies that the oxygen is closer to fluorine than to carbon atoms on the mean, and is therefore located in or near the plane of the aromatic nucleus. An approximate model is provided by the structure of liquid hexafluorobenzene proposed by Chandler and Narten,[18,19] in which the aromatic rings are located at the corners and face centers of a face-centered unit cell with the aromatic planes perpendicularly oriented to each other. The oxygen molecule could be accommodated in such a unit cell at the center of the cube, and therefore could jump from one center to another one. This model cannot account for relaxation times measured for benzene solutions, presumably because vacancies in liquid benzene are too small to freely accommodate one oxygen molecule. In this case, oxygen molecules have to continuously open their way through the liquid lattice, and their progression closely resembles a continuous translational diffusion.

It may be observed that the measured q_x values are very different for these two systems, $q_x = 60.2\ \text{s}^{-1}$ for the C_6H_6/O_2 system against $40.7\ \text{s}^{-1}$ for the C_6F_6/O_2 system. *The higher q_x value is associated to the lower oxygen solubility*, expressed as the mole number of dissolved oxygen per mole of solvent: $x_g = 8 \times 10^{-4}$ against 24×10^{-4}. The q_x parameter for these two systems is relative to the same dipolar relaxation mechanism, and to two different diffusion models, one of which—the continuous diffusion—may be considered as the asymptotic limit of the discontinuous diffusion pattern as the dimensions of the solvent cavities become smaller than those of the oxygen solute molecules. It is therefore not unreasonable to empirically compare the q_x values obtained for the carbon nuclei of the other fluorinated compounds investigated. In this respect, the magnitude of q_x will be considered as reflecting the mean value $\langle 1/r^6 \rangle$, which is thus larger for benzene than for hexafluorobenzene, as experimentally observed. The magnitude of q_x will thus be assumed to reflect the mean size of cavities and the diffusion model to be taken into consideration in the following.

Polyfluoroaromatic Solvents. Results are reported in Table III for six aromatic compounds: C_6H_6 (**1**), 1,4-$C_6H_4F_2$ (**2**), 1,3,5-$C_6H_3F_3$ (**3**), C_6F_5Cl (**4**), $C_6F_5CF_3$ (**5**), and C_6F_6 (**6**). A plot of the oxygen solubility x_g as a function of the relaxation rate coefficient q_x clearly slows a rough linearity (Figure 1) as anticipated from the above discussion. This set of compounds may be divided into three subsets: (i) compounds **1**, **2**, and **3** with very similar q_x and x_g values suggesting a common continuous translational oxygen diffusion model, (ii) compounds **5** and **6** with smaller q_x values of nearly equal magnitudes, thus suggesting a common discontinuous oxygen diffusion model, and (iii) compound **4** lying half-way from the two above subsets in the graph of Figure 1, presumably as the result of a diffusion pattern which is intermediate between the perfectly continuous and discontinuous models. The assumed existence of larger cavities in the bulk solvents by going from compounds **1** to **3** and then to **6** may be checked if we admit that the volume of these cavities may be estimated as or at least be parallel to the free volume V_f which is offered to a solute molecule in these solvents. The computation of V_f is performed in three steps, using available data from the literature. The volume of the unit cell $V_c^{(s)}$ of the solid compounds is computed from X-ray data,[19,22,23] $V_c^{(s)}$ = 507.4, 561.9, and 945 Å^3, respectively. Assuming that the solid state structure is locally maintained in the liquid state, the volume of the unit cell in the liquid state $V_c^{(l)}$ is obtained from $V_c^{(s)}$ through multiplication by the ratio of the densities of the solid and the liquid, $V_c^{(l)}$ = 592.8, 686.6, and 1153 Å^3, respectively. The validity of this procedure can be checked in the case of benzene, using small-angle X-ray data,[19] $V_c^{(l)}$ = 593.6 Å^3 (in good agreement with a computed value of 592.8 Å^3). Finally, the free volume inside the unit cell is obtained by subtracting from $V_c^{(l)}$ the volume of the solvent molecules contained in the unit cell (4, 4, or 6 in number, respectively). The volume of each solvent molecule is itself estimated as 80.4, 94.2, and 108 Å^3, respectively, using the Bondi[24] and Edward[25] increments method. The free volumes thus obtained, V_f = 271.2, 309.8, and 505 Å^3, respectively, are effectively increasing in the expected order. The existence of larger cavities within the better solvents of gaseous oxygen is also consistent with a parallel decrease of ^{19}F hyperfine constant values (Figure 2). These observations on the other hand tend to rule out the alternative assumption of a specific interaction between molecular oxygen and fluorinated solvent molecules, which should not normally result in stronger magnetic perturbations for solvents having a low solubility of oxygen as it is experimentally observed.

Aliphatic Fluorocarbons. The investigated compounds include two straight-chain fluorocarbons C_nF_{2n+2}, n = 6 and 7 (**16** and **15**), and a series of highly fluorinated molecules of the general type R_F–R_H (**11**, **13**, **14**) or R_F–R'_H–R_F (**12**, **18**) where R_F = (n-C_nF_{2n+1}, n = 6 or 8, for R_H = C_2H_5 or CH=CH$_2$ or n-C_8H_{17}, and R'_H = CH=CH or CH$_2$–CH$_2$. These compounds have been described in a previous publication[12] and are now integrated in a general comparison which was not possible at that time (Table IV and Figures 1 and 2). A striking feature for this class of fluorochemicals is a higher solubility of oxygen, again associated with smaller relaxation coefficients (Figure 1) and hyperfine coupling constants (Figure 2). A rough linear correlation is again observed between the q_x and x_g values, but the slope of the line in the aforementioned q_x–x_g plot (Figure 1) is clearly larger for the aliphatic than for the aromatic portion of the graph. Higher solubilities (and consequently smaller relaxation coefficients) are

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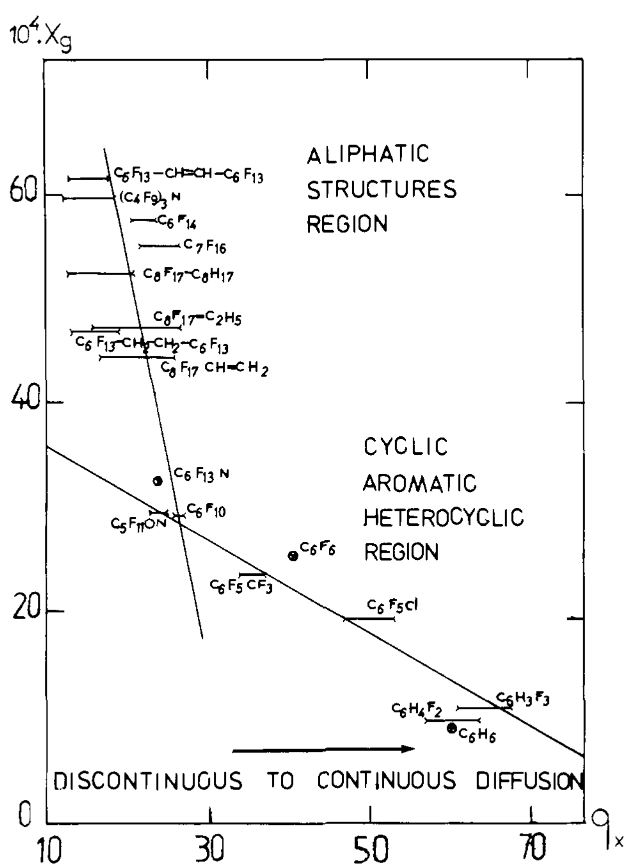

Figure 1. A graph showing the correlation between the solubility of oxygen x_g (in mole fraction) in some typical hydrocarbons and fluorochemicals and the ^{13}C relaxation coefficients q_x at 28 °C within the two classes of molecular geometries: (i) aliphatic and (ii) cyclic (aromatic, heterocyclic) structure regions (upper and lower parts of the diagram). The extremities of the segments correspond to the maximum and minimum values of q_x along the carbon skeleton of each compound. The diffusion of oxygen molecules is assumed to switch from a discontinuous to a continuous pattern by going from the left- to the right-hand side of the diagram.

not simply related to the number of fluorine atoms in each solvent molecule, thus discarding the assumption of specific fluorine–oxygen interactions. x_g and q_x values are, as for hydro- and fluoroaromatic derivatives, much larger for the aliphatic fluorocarbons than for the analogous hydrocarbons, as shown by the example of *n*-decane which was studied for the sake of comparison. All these compounds actually display a set of q_x values (minimum and maximum values only are reported in Table IV and Figure 1). Let us recall that a common feature inside each set of values is a general increase of q_x from the central to the terminal carbon nuclei. This was tentatively accounted for by the remark that the mobile extremities of the aliphatic chains cannot fit the trapped oxygen molecule as tightly as does the bulk of the perfluoroalkyl chain, thus making as many holes through the solvent shell by which the oxygen molecules are passing as they enter or leave the cavity. The average $\langle 1/r_C{}^6\rangle$ in q_x, and therefore q_x itself, is consequently higher for the terminal than for the central carbon nuclei.

If we now compare sets of values for the different perfluoroaliphatic compounds we may observe that the magnitudes of the q_x values may be classified as follows: C_6F_{14} and C_7F_{16} > $C_8F_{17}C_2H_5$ and $C_8F_{17}CH{=}CH_2$ > $C_8F_{17}C_8H_{17}$, $C_6F_{13}CH{=}CHC_6F_{13}$, and $C_6F_{13}CH_2CH_2C_6F_{13}$. This sequence is consistent with the concept of preexisting cavities in the liquid solvents, since the longer molecules (at the end of the sequence) may build up larger cavities (with smaller q_x values).

Finally, the comparison of oxygen solubilities in fluoroaromatic and fluoroaliphatic solvents suggests that aliphatic chains may build up large channels in the liquid state. On the contrary, perfectly planar structures result in closely interlocked layers of solvent molecules, as suggested by the structure of liquid benzene[19-21] (see above), which are less favorable to the inclusion solute molecules. Such a qualitative explanation may help us to understand some peculiarities observed in solubility data, as explained below.

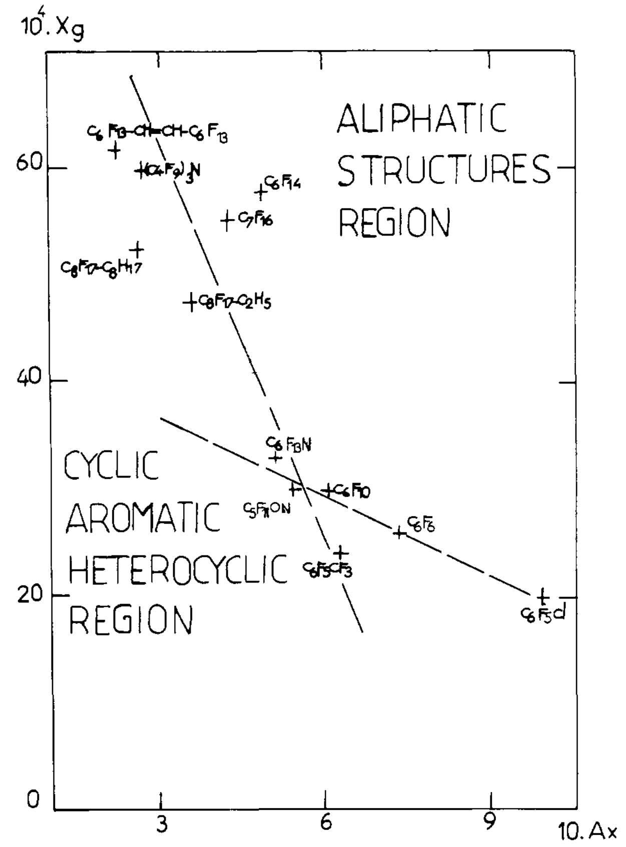

Figure 2. A similar graph as in Figure 1 showing the correlation between the oxygen solubility x_g and the ^{19}F hyperfine coupling constant in some fluorochemicals at 28 °C.

(a) The highest solubility of oxygen is reached in *trans*-bis(perfluoro-*n*-hexyl)ethylene (**18**). The comparison of **18** with its saturated analogue, the bis(perfluoro-*n*-hexyl)ethane (**12**), shows that this peculiarity should be traced to the presence of a double bond in the molecular formula of **18**. However, the maximum of solubility in **18** cannot be accounted for by the classical electronic properties of the double bond (through the formation of some charge-transfer complex with the oxygen molecule), since the presence of a *terminal double bond* in 9H,10H,10H-perfluoro-*n*-dec-9-ene (**11**) has no significant effect on the solubility of oxygen as it may be seen by comparing **11** with its saturated analogue $C_8F_{17}C_2H_5$ (**13**). The important point is therefore the *central* position of the *trans* olefinic bond in the alkyl chain inducing the existence of a "notch" in the solvent cavities which may facilitate both the inclusion of an oxygen molecule (hence higher x_g and lower q_x values in **18** than in **12**) and its diffusion outside the cavity (hence the maximum of q_x along the carbon skeleton which is observed for the ethylenic carbons of **18**, and not for the ethanic carbons of **12**).

(b) Perfluorotributylamine is also characterized by a high solubility of oxygen, and aqueous emulsions of this compound have been presented as a potential blood substitute.[10] The diffusivity of gases in this solvent, as well as its fluidity and degree of expansion as a function of temperature, have been recognized as highly unusual by Hildebrand.[26] Small gaseous molecules, such as H_2 or Ne, were found to continue to diffuse even at temperatures where the solvent was highly viscous. This was traced to

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(26) J. H. Hildebrand and R. H. Lamoreaux In "Viscosity and Diffusivity", J. H. Hildebrand, Ed., Wiley, New York, 1977, Chapter 8, and references therein.

the fact that "small molecules find channels for diffusion between the interlocked cogwheel-like molecules of perfluorotributylamine". These views fairly support our own picture of gas solubility in perfluorochemicals.

(c) A methyl group (or a small chain) branched on a straight-chain perfluorocarbon may be imagined as the equivalent of a methane molecule attached to the wall of the channel-like cavity in the liquid, thus decreasing the free space in the cavity to accommodate oxygen molecules. Such a picture would account for the strong decrease of solubility observed by going from normal perfluorohexane (**16**) to perfluoro-3,4-dimethylhexane (**19**), $x_g = 57.6$ and 35.2×10^{-4}, respectively. This model can also account for the net increase of viscosity between these two compounds, 0.66 and 1.60 cP at 25 °C, respectively, since the lateral methyl blocks in **19** prevent the thread-like alkyl chains from sliding easily on each other.

Cyclic Compounds

A last piece of evidence supporting these views is brought about by the study of three cyclic compounds: perfluorocyclohexene (**7**), -*N*-methylpiperidine (**8**), and -*N*-methylmorpholine (**9**). For each of them, the carbon nuclei of their oxygen solution have nearly equal q_x coefficients, thus showing that the carbon nuclei in each compound are equally perturbed by the presence of nearby paramagnetic oxygen molecules (Table V). Moreover, the presence of a heterocyclic nitrogen atom in **8**, of an ethylenic bond in **7**, or of nitrogen and oxygen atoms in **9** has no significant influence on q_x (and x_g) values which are nearly constant all along this series of compounds. This again points to the absence of any specific solute–solvent interaction. These remarks again lead us to the conclusion that perfluorinated solvent molecules behave like hard space-filling blocks which can accommodate small gaseous molecules in the free space left available between them. This means that geometrically related molecules are characterized by similar dissolving properties toward gases. If we now compare molecules of widely different geometries, thread-like molecules such as aliphatic fluorochemicals are naturally inclined to locally orient themselves parallel to each other (as shown by the possibility of a long-range ordering of this type in liquid crystals), thus creating large channel-like cavities in the liquid state. Cyclic molecules, however, may result in closer packings which are less favorable to the insertion of solute molecules. In this respect, gauche structures as in the three cyclic compounds examined presently are expected to give rise to less ordered packings than planar aromatic molecules. These considerations account for the order of decreasing q_x or A_x values (or conversely of increasing solubilities) which is observed on the graphs of Figures 1 and 2: aromatic > cyclic (nonaromatic) > aliphatic.

In conclusion, the structure of the fluid alone seems to be the predominant factor in accounting for the solubility of gases in fluorochemicals, whatever the other structural details may be. This is in line with Chandler's view[27] that the structure of nonassociated nonpolar liquids such as fluorochemicals or hydrocarbons mainly depends on *the shape of the molecules*. The presence of fluorine atoms bordering the carbon chain in fluorocarbons, which are larger than hydrogen atoms in hydrocarbons, results in more irregular molecular shapes, and therefore in the existence of numerous large-sized cavities in the liquid, thus explaining their ability to dissolve significant quantities of gases. Such a picture is also in agreement with the aforementioned exceptional properties of the pure liquids: lower boiling points, surface tensions, and isothermal compressibility factors.

In this respect, it has been pointed out[1] that the energy of activation for viscous flow *E* in liquid normal perfluoroheptane is approximately one-sixth of the energy of vaporization, while for the analogous hydrocarbon, *E* is only one-sixteenth of the energy of vaporization. This was traced to additional attraction in hydrocarbons in the frame of the cell theory of liquids. Unusually high forces of attraction between molecules that contain hydrogen atoms, especially in hydrocarbons, brings molecules closer together than normal. Consequently the compressibility of hydrocarbons is higher, the liquid viscosity lower, the energy of activation for viscous flow higher, and *the solubility of gases lower* than would be found for the physical properties in the absence of this extra interaction *as in fluorocarbons*.

As the microscopic state of the liquid solvent also controls macroscopic properties such as viscosity, heats of vaporization, molar volumes, Hildebrand solubility parameters,..., there may exist correlations between gas solubilities and any of these parameters.[6,7] However the microscopic description given above shows that these parameters cannot be related quantitatively in a straightforward manner and that the correlations thus obtained are always restricted to a series of structurally related compounds. Parameters of importance are in fact the number and size of cavities in the liquid solvents. The number of cavities is probably roughly proportional to the number of solvent molecules, so that the solubility per mole of solvent (x_g) is mainly determined by the size of the cavities. The general correlation between q_x (or A_x) and x_g values strongly suggests that the inverse magnitude of q_x effectively reflects the size of these cavities.

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