Solubilities of Buckminsterfullerene and Sulfur Hexafluoride in Various Solvents

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The solubilities of buckminsterfullerene, C_{60}, at 298 and 303 K and of sulfur hexafluoride, SF_6, at 298 K in various solvents, obtained from the literature, were submitted to stepwise linear regression analysis with respect to the relevant solvent properties. Different sets of properties were found to govern the solubilities of these two substances. In the case of C_{60} the solvent polarizability (expressed by the molar refraction and the π^* solvatochromic parameter) helps the solubility and the solvent polarity (expressed by the dipole moment and the $E_T(30)$ solvatochromic parameter) counteracts it. On the contrary, the solubility of SF_6 is mainly affected (adversely) by the surface tension of the solvent, and somewhat assisted by its polarizability and hampered by its polarity. These findings are rationalized in terms of the physicochemical interactions that take place in these systems.

Introduction

Globular molecules have attracted a great deal of attention, since in many respects their spherical shape lends them a greater facility to be treated by means of theoretical approaches than have oblate or prolate molecules. Buckminsterfullerene, C_{60}, is an especially appropriate example of a globular molecule (nearly perfectly spherical but actually a truncated icosahedron), and indeed it has been discussed from many aspects since its discovery a few years ago. One of the properties that require explanation is its highly individual solubility in a variety of solvents. A high solubility is necessary for efficient separation of C_{60} from other fullerenes present in soot, from which it is manufactured. Ideally, a knowledge of the properties of solvents that are conducive to a high solubility can help in the selection of optimal conditions for the preparation of pure C_{60}, as noted by Ruoff et al.[1] in a recent paper. They also mentioned that few data were available on the solubility of molecules that both form van der Waals solids and are round, so that comparison of the solubility of C_{60} with that of analogous systems was not possible.

Sulfur hexafluoride, SF_6, forms a van der Waals solid, and although an octahedral molecule it approximates sphericity to a sufficient extent to be able to be treated as such. Of these two substances, C_{60} is a solid and SF_6 a gas at ambient conditions, but both are globular and large, having been ascribed diameters of 1003 pm[2] and 530 pm,[3] respectively. They are nonpolar and interact by dispersion forces with neighboring molecules. It is, therefore, of interest to compare the solubilities of C_{60} and SF_6, to see whether similar sets of solvent properties are operative in providing for a high solubility. Superficially, they should not differ much in their solubility behavior, but as will be seen, this presumption is wrong.

The solubility of the SF_6 in various solvents has been reported and discussed in terms of the solvent properties involved by several authors.[3−5] A comprehensive compilation of solubility data for C_{60} has only very recently become available,[6] and two recent papers discussed this subject in relation to the properties of the solvents.[1,7] These papers tried to select a single solvent property that ought to be the major, if not exclusive, cause for high solubility of these substances, but have not been particularly successful in this.

Solubility, being a Gibbs free energy related property, can be treated by means of linear free energy relationships (LFERs). In fact, Ruoff et al.[1] mentioned the possibility of applying multivariate statistical methods to this problem but refrained from doing so. One method that has proved successful for relating solution data for a set of solvents to their properties is the application of stepwise multivariate linear regression analysis to the data for modeling the system.[8] In this method, relevant properties of the solvents are selected sequentially as independent variables and permitted to enter and forced to exit the regression according to provided statistical criteria. The final set of properties retained then define the model for the system and "explain" the variance of the dependent variable (the solubility in our case) to as high an extent as the system permits. The properties employed as independent variables need to be mutually uncorrelated: their (absolute) correlation coefficient should ideally be <0.5. It then remains to rationalize the statistically obtained dependence in terms of the physicochemical interactions that take place in the system studied. That is, it is necessary to explain why certain properties have been selected to describe what takes place whereas others are deemed not to be of importance.

In the case of the solubility of a given solute in a set of solvents, the following solvent properties are considered to be relevant. The solubility of many nonelectrolyte solutes (subscript 2) in nonpolar solvents (subscript 1) is generally describable[7,9] by means of the solubility parameters δ:

$$\log x_2 = -(RT \ln 10)^{-1} \phi_1^2 V_2 [\delta_1 - \delta_2]^2 \qquad (1)$$

where x denotes mole fraction, ϕ volume fraction, and V molar volume. Note that for low solubilities, as encountered here, the factor ϕ_1^2 on the rhs is approximately unity. Opening the brackets then leads to a dependence on both δ_1 and δ_1^2. However, these two quantities are well correlated, and only one of them is required in the regression.

Other physical properties of the solvents are also relevant, their values (as well as that of δ) being taken mostly from the compilation of Riddick et al.[10] One such property is the number of solvent molecules that can pack around a solute molecule and interact with it,[1] and it depends inversely on the size of the former, as represented by the molar volume, V_1. The solubility of fullerene has been compared with that of inert gases,[7] and it

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was shown[11] that the solubility of inert gases in molten salts can be described in terms of the work done when a macroscopic body is introduced into the liquid, despite the microscopic size of the hole being created by the solute. This work depends on the surface tension, γ_1, of the solvent, which is, therefore, also one of the variables tested. Structuredness of the solvent, measured by $[C_{p1}(l) - C_{p1}(g)]/V_1$,[12] where C_p is the molar heat capacity of the liquid (l) or vapor (g), that would have a detrimental effect on the solubility, again in connection with the work required for the creation of a hole, is another such variable.

The dipole moment of the solvent molecules, μ_1, is expected to be relevant to interactions with induced dipoles in the solute. The polarity, given by the Clausius−Mosotti expression

$$P_1 = V_1(\epsilon_1 - 1)/(\epsilon_1 + 2) \tag{2}$$

where ϵ is the relative permittivity, can describe this property from another aspect.[1] The two quantities μ and P need not be correlated, since the latter involves a cooperative property of the solvent molecules, but P might be correlated with V for a related set of solvents. The polarizability α_1 of the solvent molecules can also be involved,[1] described by the molar refraction $R_1 = (4\pi/3)N_{Av}\alpha_1$, obtained in turn from the refractive index, e.g. at the sodium D line, n_D, according to the Lorentz−Lorenz expression

$$R_1 = V_1(n_{D1}^2 - 1)/(n_{D1}^2 + 2) \tag{3}$$

More specific interactions of the solvents with the solutes can be described by means of certain solvatochromic parameters, measuring the polarity, polarizability, and hydrogen bond donation and acceptance abilities of the solvents. A manifestation of the LFER applicable to solubilities is the Kamlet−Taft[13] expression:

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \tag{4}$$

Here XYZ is the free energy related property, π^*, α, and β are solvent properties, while XYZ_0, s, a, and b are solvent-independent solute/system properties. The polarity/polarizability π^* parameter and the hydrogen-bond-donation ability α parameter should be relevant in the present context, the latter since it is connected with the self-association behavior of the solvents, hence with the work required to create a cavity for the accommodation of the solute. It is not expected that the solvent hydrogen-bond-acceptance ability (described by the β parameters) plays any role in the present case of the globular non-hydrogen-bond-donating solutes. The Dimroth−Reichardt polarity index $E_T(30)$ has been shown to explain many solvent-dependent interactions.[14] This quantity has been shown[15] to depend on the α of the solvents as well as on their π^*, but in a manner that does not necessarily make these three quantities mutually well correlated.

The set of independent variables obtained from the literature, describing the properties of the solvents dealt with here, is shown in Table 1.

Results

The solubilities are described herein by the (decadic) logarithm of the mole fraction of the solute, $\log x_2$, in the saturated solution at the given temperature T (and a partial pressure of 101.325 kPa (1 atm), the Henry's law constant, in the case of the gaseous SF_6). Some of the data for C_{60} are available[6] in terms of mg/mL, and these are converted to x_2 by multiplication by $V_1/(720.66 \times 1000)$. Here V_1 is in cm^3 mol^{-1} and 720.66 g

mol^{-1} is the molar mass of the fullerene, the solubilities being sufficiently small for this expression to be valid.

The solubility of buckminsterfullerene, C_{60}, was obtained at 298 K from the review of Beck and Mandi[6] (at 293−298 K for data from Ruoff et al.[1]), which cites the sources of the data and discusses their reliability. It was assumed that the solid at equilibrium with the saturated solution at room temperature and above it was pure, unsolvated, C_{60} (but see the Discussion). The values of $\log x_2$ were the dependent variable for the regression analysis, with the properties listed above used as the independent variables. Unfortunately, the entire set of 120 different solvents for which the solubility data have been compiled could not be used, for two reasons. For a few (nitromethane, acetonitrile, and possibly also water and methanol) the solubility is so low that it is given as zero, so that $\log x_2$ is indeterminate for practical purposes. For many other solvents, the required values for the independent variables (solvent properties) are not given in readily available sources.[10,12,13] The subset of usable solvents, therefore, comprises 61 solvents only, but these include most of the common classes of solvents: aliphatic and aromatic hydrocarbons, their halogen derivatives, alcohols, some polar aliphatic and aromatic solvents, and a few nitrogen- and sulfur-containing solvents.

The Crunch version 4.0 stepwise regression program was employed for the statistical analysis of the data, with a Fischer statistic $F = 1$ as a criterion for entry or rejection. Of the above-described list of independent variables the program rejected most and accepted only four: the molar refraction R (in cm^3 mol^{-1}), the polarity/polarizability parameter π^*, the polarity parameter $E_T(30)$ (in kcal mol^{-1}, 1 cal = 4.184 J), and the dipole moment μ (in debyes, 1 D = 3.33564×10^{-30} C m), in decreasing order of importance. The resulting expression for the best model is

$$\log x_2 = -(4.58 \pm 0.59) + (7.72 \pm 0.84)10^{-2}R +$$
$$(2.53 \pm 0.30)\pi^* - (8.05 \pm 1.27)10^{-2}E_T(30) -$$
$$(0.190 \pm 0.080)\mu \quad (5)$$

It describes the subset of solvents (from which the outlyers, see below, have been "filtered" off) with a multiple correlation coefficient $R_{corr} = 0.9328$, an adjusted $R_{corr}^2 = 0.8590$ (i.e., ~86% of the variance is "explained" by eq 5), a standard error $\sigma = 0.40$, and a Fischer $F_{4,48} = 79$ for the $n = 55$ remaining solvents. The outlyers (decane, hexadecane, carbon disulfide, diiodomethane, 1-butylamine, and nitroethane) deviated by $>2\sigma$. The quality of the fit of eq 5 is shown in Figure 1a. Table 2 lists the mutual correlation coefficients and the percent of the variance accounted for by the independent variables in the model. The experimental and calculated values of $-\log x_2$ are shown in Table 3.

The solubility of C_{60} at 303 K is also available[6,7] for a fairly large set of solvents, $n = 20$, to which the stepwise regression can be applied. The same comprehensive set of properties was offered to the statistical program as for the data at 298 K, with the following results, where most variables were again rejected:

$$\log x_2 = (3.59 \pm 3.31) + (3.46 \pm 1.08) \times 10^{-2}R +$$
$$(5.10 \pm 0.91)\pi^* - (31.7 \pm 10.2) \times 10^{-2}E_T(30) \quad (6)$$

without the need for a term in μ to maximize the fit. In this case the multiple correlation coefficient $R_{corr} = 0.8732$, an adjusted $R_{corr}^2 = 0.7179$ (i.e., ~72% of the variance is "explained" by eq 6), a standard error $\sigma = 0.52$, and a Fischer $F_{3,17} = 17$ were obtained for the fit. The worse results are explained by the lower diversity of the solvents, their being practically all nonpolar (hence the absence of the dipole moment term) aliphatic and aromatic hydrocarbons and halogen-

TABLE 1: Properties of the Solvents Used in the Regressions[a]

solvent	V	δ	γ	μ	ϵ	n_D^2	α	π^*	$E_T(30)$	struct
n-pentane	116.1	14.4	15.5	0.00	1.84	1.843	0.00	−0.15	31.1	0.41
n-hexane	131.6	15.0	17.9	0.00	1.88	1.883	0.00	−0.11	31.0	0.40
n-heptane	147.5	15.2	19.7	0.00	1.92	1.925	0.00	−0.06	31.1	0.41
n-octane	163.5	15.5	21.2	0.00	1.95	1.946	0.00	0.01	31.1	0.41
i-octane	160.4	14.7	18.3	0.00	1.96	1.962	0.00	0.01	31.0	0.31
n-decane	195.9	15.8	23.4	0.00	1.99	1.987	0.00	0.03	31.0	0.42
n-dodecame	228.6	16.0	24.9	0.00	2.00	2.015	0.00	−0.01	31.1	0.43
n-tetradecane[b]	260.5	16.2	26.0	0.00	2.03	2.034	0.00	0.06	31.0	0.44
n-hexadecane[c]	294.1	16.3	27.1	0.00	2.05	2.052	0.00	0.08	31.0	0.45
c-hexane	108.7	16.8	24.6	0.00	2.02	2.026	0.00	0.00	30.9	0.46
methyl-*c*-hexane[c]	128.3	16.0	23.3	0.00	2.02	2.018	0.00	0.00	31.0	0.39
cis-decalim	154.8	17.8	31.6	0.00	2.20	2.187	0.00	0.09	31.2	0.42
benzene	89.9	18.8	28.2	0.00	2.27	2.244	0.00	0.55	34.3	0.45
toluene	106.9	18.8	27.9	0.31	2.38	2.232	0.00	0.49	33.9	0.61
o-xylene	121.2	18.0	29.5	0.45	2.57	2.259	0.00	0.51	34.7	0.50
m-xylene	123.4	18.0	28.1	0.30	2.37	2.234	0.00	0.47	34.6	0.44
p-xylene	123.9	18.1	27.8	0.00	2.27	2.230	0.00	0.45	33.1	0.45
ethylbenzene	123.1	18.0	28.5	0.37	2.40	2.051	0.00	0.53	34.1	0.46
mesitylene	139.6	18.1	28.3	0.00	2.28	2.240	0.00	0.45	32.9	0.34
cumeme	140.2	17.6	27.7	0.39	2.38	2.217	0.00	0.41	34.6	0.47
perfluoroheptane	224.6	12.3		0.00	1.77	1.593	0.00	−0.39		
perfluoro-Me-*c*-hexane	195.8	12.7		0.00	1.85	1.634	0.00	−0.48		
fluorobenzene	94.3	18.1	27.1	1.48	5.42	2.156	0.00	0.62	37.0	0.55
hexafluorobenzene[d]	115.8	16.9	21.6	0.00	1.89	1.890	0.00	0.27	34.2	0.56
dichloromethane	64.5	20.2	27.2	1.14	8.93	2.020	0.13	0.82	40.7	0.78
chloroform	80.7	19.5	26.5	1.15	4.89	2.082	0.20	0.58	39.1	0.64
tetrachloromethane	97.1	17.6	26.1	0.00	2.24	2.124	0.00	0.21	32.4	0.49
1,2-dichloroethane	79.4	20.0	31.5	1.83	10.36	2.080	0.00	0.73	41.3	0.65
1,1,1-trichloroethane	100.3	19.6	24.9	1.70	7.25	2.062	0.00	0.44	36.2	0.52
1,1,2,2-tetrachloroethane	105.8	20.2	35.4	1.71	8.20	2.224	0.00	0.95	39.4	0.63
trichloroethylene	90.0	19.0	28.8	0.80	3.42	2.176	0.00	0.48	35.9	0.47
tetrachloroethylene	102.7	19.0	31.3	0.00	2.28	2.260	0.00	0.25	32.1	0.50
1-chloropropane	88.9	17.4	21.1	1.97	7.70	1.844	0.00	0.43	37.4	0.53
1,2,3-trichloropropane	106.6	20.6	37.1	1.85	7.45	2.194	0.00	0.78	40.4	0.56
chlorobenzene	102.2	19.8	32.5	1.69	5.62	2.317	0.00	0.68	36.8	0.50
o-dichlorobenzene	113.1	20.5	36.2	2.50	9.93	2.400	0.00	0.77	38.0	0.96
m-dichlorobenzene	114.6	20.0	35.5	1.54	5.04	2.382	0.00	0.65	36.7	0.42
1,2,4-trichlorobenzene	124.8	20.7	44.7	1.26	4.15	2.468	0.00	0.66	36.2	0.44
dibromomethane	69.8	22.4	40.1	1.43	6.68	2.377	0.00	0.92	39.4	0.70
bromoform	87.8	21.9	45.0	0.99	4.39	2.546	0.00	0.62	37.7	0.70
1,2-dibromoethane	86.6	19.8	38.3	1.19	4.75	2.359	0.00	0.75	38.3	0.71
1-bromopropane	91.4	18.2	25.2	1.93	8.09	2.050	0.00	0.49	36.9	0.59
bromobenzene	105.5	20.2	35.5	1.56	5.40	2.424	0.00	0.77	36.6	0.52
diiodomethane	80.6	24.1	50.0	1.08	5.32	3.083	0.00	1.00	36.5	0.95
1-iodopropane	97.7	18.6	29.0	1.84	7.00	2.258	0.00	0.60	35.7	0.61
iodobenzene	111.9	20.7	38.8	1.40	4.49	2.615	0.00	0.84	36.2	0.52
water	18.1	47.9	71.8	1.85	78.36	1.776	1.17	1.09	63.1	2.31
methanol	40.7	29.3	22.3	2.87	32.66	1.760	0.98	0.60	55.4	0.92
ethanol	58.7	26.0	21.9	1.66	24.55	1.848	0.86	0.54	51.9	0.80
1-propanol	75.1	24.4	23.1	3.09	20.45	1.915	0.84	0.52	50.7	0.76
1-butanol	92.0	23.3	24.2	1.75	17.51	1.952	0.84	0.47	49.7	0.73
1-pentanol	108.5	22.4	25.2	1.70	13.90	1.982	0.84	0.40	49.1	0.70
1-hexanol	125.2	21.8	25.7	1.55	13.30	2.005	0.80	0.40	48.8	0.68
1-octanol	158.4	20.9	26.9	1.76	10.34	2.038	0.77	0.40	48.1	0.66
1-decanol	191.0	19.9	28.4	1.62	8.10	2.064	0.70	0.45	47.7	
1,2-ethanediol	55.9	32.4	47.4	2.31	37.70	2.047	0.90	0.92	56.3	0.92
o-cresol[e]	104.0	21.9	35.0	1.45	11.50	2.344	1.65	0.68	51.9	0.96
tetrahydrofuran	81.6	19.0	26.4	1.75	7.58	1.974	0.00	0.55	37.4	0.58
1,4-dioxane	85.7	19.7	32.8	0.45	2.21	2.017	0.00	0.49	36.0	0.66
anisole	109.3	19.7	34.6	1.25	4.33	2.293	0.00	0.70	37.1	
acetone	74.0	22.1	22.7	2.69	20.56	1.839	0.08	0.62	42.2	0.68
propylene carbonate	85.2	21.8	41.4	4.94	64.92	2.019	0.00	0.83	46.0	
1-aminobutane	99.3	17.8	23.5	1.37	4.88	1.956	0.05	0.31	37.6	0.71
nitromethane	54.0	25.7	36.3	3.56	35.87	1.903	0.22	0.75	46.3	0.90
nitroethane	71.9	22.7	32.1	3.60	28.06	1.931	0.00	0.77	43.6	0.78
nitrobenzene	102.7	22.1	42.4	4.22	34.78	2.403	0.00	0.86	41.2	0.49
acetonitrile	52.9	24.1	28.3	3.92	35.94	1.800	0.19	0.66	45.6	0.74
benzonitrile	103.1	22.7	38.5	4.18	25.20	2.328	0.00	0.88	41.5	0.79
pyridine	80.9	21.7	36.3	2.37	12.91	2.273	0.00	0.87	40.5	0.69
quinoline	118.5	22.8	45.2	2.18	8.95	2.640	0.00	0.93	39.4	0.58
N-methylformamide	59.1	31.1	39.5	3.86	182.40	2.045	0.62	0.90	54.1	0.88
N,N-dimethylformamide	77.4	24.1	36.4	3.92	36.71	2.024	0.00	0.88	43.2	0.74
N,N-dimethylacetamide	93.0	23.3	31.7	3.72	37.78	2.061	0.00	0.85	42.9	0.72
N-methylpyrrolidinone	96.4	23.6	40.7	4.09	32.20	2.155	0.00	0.92	42.2	0.64
hexamethyl phosphoramide	175.1	19.1	33.8	5.54	29.30	2.123	0.00	0.87	40.9	
carbon disulfide	60.6	20.3	31.5	0.06	2.64	2.638	0.00	0.51	32.8	0.50
tetrahydrothiophene	88.7	20.5	35.0	1.90	8.61	2.257	0.00	0.60	36.8	0.55
dimethylsulfoxide	71.3	26.6	43.0	4.06	46.45	2.182	0.00	1.00	45.1	0.89

[a] The data, unless otherwise noted, for volume (V/cm³ mol⁻¹), δ (J^{1/2} cm^{−3/2}), γ ($10^{−2}$ N m⁻¹), μ (D), ϵ, and n_D^2 are from ref 10; those for α and π^* are from ref 13 or from ref 19; those for $E_T(30)$ (kcal mol⁻¹) are from ref 14; those for struct ($[C_P(l) − C_P(g)]/V$/J K⁻¹ cm⁻³) are from ref 12. [b] The data for tetradecane were taken to be the means of those for dodecane and hexadecane. [c] The data for hexadecane are from DIPPR, *Numerica*, Tech. Data Services, New York, Vers. 1.0, 1988; the π^* and $E_T(30)$ values are estimated from those of other alkanes and cycloalkanes. [d] The ϵ value was set equal to n_D^2. [e] The α values were estimates as equal to that of phenol.
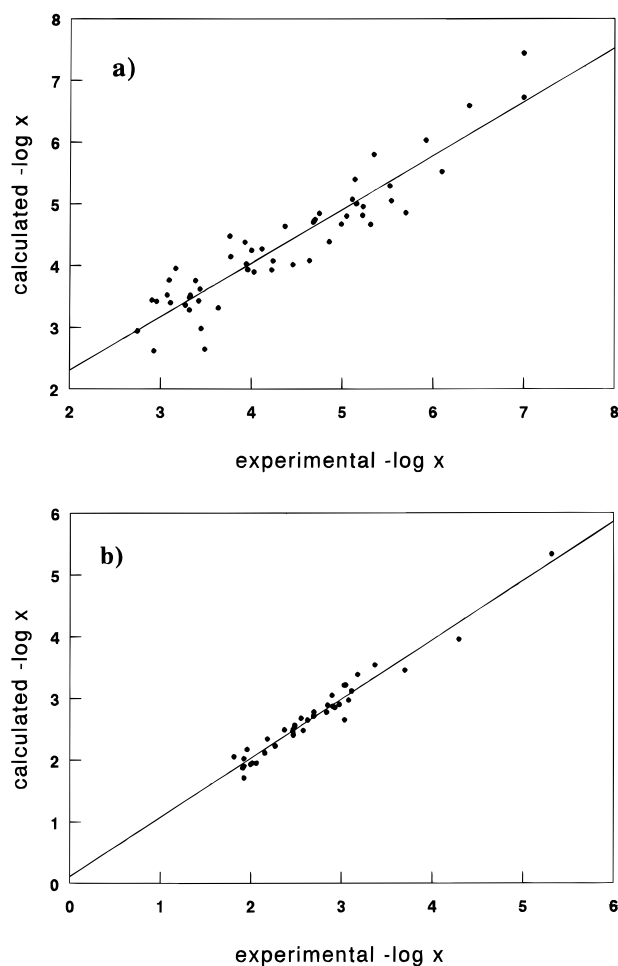
Figure 1. Calculated vs experimental values of the $-\log x_2$ values for the solubilities at 298 K of (a) C_{60} and (b) SF_6.

TABLE 2: Mutual Correlation Coefficients for the Independent Variables in the Model Describing the Solubility of C_{60} and the Percent of the Solubility Variance Accounted for by Them

variable	π^*	$E_T(30)$	μ	% of variance
R	−0.158	0.347	0.110	56.4
π^*		0.007	−0.595	10.3
$E_T(30)$			−0.447	18.8
μ				1.6

substituted hydrocarbons, together with carbon disulfide, tetrahydrothiophene, and the ethers 1,4-dioxane and tetrahydrofuran. The experimental and calculated values of $-\log x_2$ are shown in Table 4.

The available solubility data for sulfur hexafluoride, SF_6, at 298 K have been summarized by Brückl and Kim,[3] who cited their sources when not determined by them. A few additional data by Wilcock et al.[16] (octanol and decanol) and Scharlin and Battino[17] (water and D_2O) are also included. There are 38 solvents for which solubility data as well as values of the solvent properties are available, including the same classes of solvents as for C_{60} at 298 K, but many more polar solvents and fewer halogen-substituted aliphatic hydrocarbons. The regression in this case gave the following expression for the best model, involving the surface tension (in N m^{-1}), the molar refraction R (in cm^3 mol^{-1}), and the polarity $E_T(30)$ (in kcal mol^{-1}):

$$\log x_2 = -(0.734 \pm 0.181) - (4.59 \pm 0.31) \times 10\gamma +$$
$$(1.07 \pm 0.19) \times 10^{-2}R - (2.13 \pm 0.42) \times 10^{-2}E_T(30) \quad (7)$$

with a multiple correlation coefficient $R_{corr} = 0.9786$, an adjusted

$R_{corr}^2 = 0.9538$ (i.e., ~95% of the variance is "explained" by eq 7), a standard error $\sigma = 0.15$, and a Fischer $F_{3,35} = 256$. The quality of the fit of eq 7 is shown in Figure 1b. Table 5 lists the mutual correlation coefficients and the percent of the variance accounted for by the independent variables in the model. The experimental and calculated values of $-\log x_2$ are shown in Table 6.

The solubilities of C_{60} and SF_6 at 298 K are compared in Figure 2 for those solvents where data for both substances are available.

Discussion

When the solubilities of a given solute in different solvents are compared, it is customary to do so isothermally, i.e., at a given temperature, whether the process of dissolution is endo- or exothermic. That is, the Gibbs free energies of the dissolution process are compared, by means of linear (Gibbs) free energy relations (LFERs), not its enthalpies. It is noteworthy that with some solvents (aromatic ones,[18−21] possibly also carbon disulfide[20,21]) C_{60} forms crystal solvates at low temperatures and that these dissociate (presumably to the bare, unsolvated[18,19] C_{60}) at higher ones. This behavior manifests itself by a (sharp) maximum in the $x_2(T)$ curve.[1,18,21] For most of the solvents of concern here this maximum, if it exists, is at <298.15 K,[6] where the correlation (5) applies. The following discussion is based on the assumption that at ≥298.15 K the solid C_{60} that is at equilibrium with the saturated solutions is, in fact, the unsolvated C_{60}. If and when data are found for certain solvents that contradict this assumption, these have to be removed from the database and possibly the correlation has to be modified. In any case, the present analysis does not refer explicitly to the enthalpy and entropy changes that take place on dissolution of the C_{60}, which depend not only on the direct interactions of the solvents with the solute but also on rearrangements of the solvent−solvent interactions in the surroundings of the solute.

The quality of the fit of eq 5 to the C_{60} solubility data is far from perfect (see Figure 1a); that is the model fails to account for the entire variance of the set of solvents, but it does account for the major fraction of it (~86%). It must be noted that the data for a given solvent obtained by different authors show large discrepancies themselves; for example, at 298 K the values are reported[6] as 0.54 and 2.80 mg/mL for toluene and as 7.11 and 24.6 mg/mL for 1,2-dichlorobenzene. Difficulties with the quality of the data, due to slowness of attaining equilibrium and imperfect purity of the fullerene, have been discussed in the review.[6] The standard deviation of the model, $\sigma = 0.40$ for log x_2, corresponds to a factor of 2.5 for the solubilities themselves, and all the calculated solubilities (except the outlyers) were within 2σ, i.e., within a factor of ~6 from the experimental ones.

In the cases of some outlyers the discrepancies can be understood. The long-chain alkanes, decane, and hexadecane have very large molar refractivities, beyond all other solvents in the set, due to the large molar volumes, leading to much too large calculated solubilities. Still, the direction of the increasing solubilities, from 0.005[1] via 0.043[1] and 0.071[1] to 0.15[2] mg/mL for pentane, hexane, decane, and hexadecane, respectively, is not explained by the increase in π^* alone (from −0.15 to 0.08 in this series) but requires a contribution related to the molar volume, such as R. The increasing amount of void space in this series of alkanes (see below) can be the answer to this problem.

The large solubility reported[6] for 1-butylamine at 298 K (log $x_2 = -3.30$) is inconsistent with the trend at 308 and 318 K (log $x_2 = -3.71$ and −3.86, respectively), but this is insufficient to explain why in this polar solvent ($\mu = 1.37$ D) C_{60} is so

TABLE 3: Experimental and Calculated [Eq 5] Solubilities ($-\log x_2$) of C$_{60}$ at 298 K in Various Solvents

solvent	exptl	calcd	solvent	exptl	calcd
n-pentane	6.10	5.52	bromoform	3.17	3.96
n-hexane	5.11	5.08	1,2-dibromoethane	4.22	3.93
n-octane	5.25		1-bromopropane	5.22	4.87
n-decane	4.72		bromobenzene	3.32	3.28
c-hexane	5.23	4.96	diiodomethane	4.82	
cis-decalin	3.33	3.52	1-iodopropane	4.64	4.08
benzene	3.96	3.94	iodobenzene	3.49	2.65
toluene	3.38	3.76	methanol	7.30	7.44
o-xylene	2.91	3.44	ethanol	7.00	6.72
m-xylene	3.32	3.49	1-propanol	6.40	6.59
p-xylene	3.27	3.36	1-butanol	5.92	6.03
ethylbenzene	3.43	3.62	1-pentanol	5.35	5.80
mesitylene	3.45	2.98	1-hexanol	5.14	5.40
cumene	3.64	3.32	1-octanol	4.99	4.67
fluorobenzene	4.11	4.27	o-cresol	5.70	4.86
dichloromethane	4.70	4.75	tetrahydrofuran	5.16	5.01
chloroform	4.75	4.85	1,4-dioxane	5.31	4.67
tetrachloromethane	4.37	4.64	anisole	3.07	3.53
1,2-dichloroethane	5.05	4.80	1-aminobutane	3.30	
1,1,1-trichloroethane	4.68	4.71	nitroethane	6.70	
trichloroethylene	3.76	4.48	nitrobenzene	3.94	4.03
tetrachloroethylene	3.77	4.15	benzonitrile	4.24	4.08
1-chloropropane	5.52	5.29	pyridine	4.00	4.25
1,2,3-trichloropropane	4.03	3.90	quinoline	2.93	2.62
chlorobenzene	3.10	3.77	N,N-dimethylformamide	5.54	5.05
o-dichlorobenzene	2.96	3.42	N-methylpyrrolidinone	3.93	4.38
m-dichlorobenzene	3.42	3.43	carbon disulfide	3.18	
1,2,4-trichlorobenzene	2.75	2.94	tetrahydrothiophene	4.85	4.39
dibromomethane	4.46	4.02			

TABLE 4: Experimental and Calculated [Eq 6] Solubilities ($-\log x_2$) of C$_{60}$ at 303 K in Various Solvents

solvent	exptl	calcd	solvent	exptl	calcd
n-pentane	6.22	6.16	o-xylene	2.76	3.57
n-hexane	5.14	5.77	mesitylene	3.71	3.14
n-octane	5.25	4.87	dichloromethane	4.64	4.57
i-octane	5.23	4.88	tetrachloromethane	4.22	4.70
n-decane	4.72	4.41	o-dichlorobenzene	2.70	3.29
n-dodecane	3.54	4.33	1,2,4-trichlorobenzene	2.80	3.10
n-tetradecane	4.34	3.72	tetrahydrofuran	4.83	4.77
c-hexane	5.14	5.25	1,4-dioxane	5.31	4.58
benzene	3.75	3.57	carbon disulfide	3.37	3.47
toluene	3.50	3.59	tetrahydrothiophene	4.72	4.11

TABLE 5: Mutual Correlation Coefficients for the Independent Variables in the Model Describing the Solubility of SF$_6$ and the Percent of the Solubility Variance Accounted for by Them

variable	R	$E_T(30)$	% of variance
γ	-0.028	-0.546	81.7
R		0.492	11.3
$E_T(30)$			0.3

much more soluble than in other polar solvents. Another discrepancy noted is the low solubility reported[6] in diiodomethane ($\log x_2 = -4.82$), relative to dichloro- ($\log x_2 = -4.64$) and dibromomethane ($\log x_2 = -4.46$), whereas for other halo-substituted alkanes the solubility increases from chloro- to bromo- to iodo-substituted solvents. Nitroethane is one of the polar solvents permitting only a very low solubility of C$_{60}$, which is reported to only one significant figure (0.002 mg/mL), thus accounting for a large possible error. However, eq 5 predicts considerably higher solubilities of C$_{60}$ in some polar solvents (acetone, acetonitrile, nitromethane, nitroethane, methanol) than reported,[1,6] whereas in other polar solvents (such as the higher alkanols, pyridine, N-methylpyrrolidinone, N,N-dimethylformamide) the predicted values are within the standard deviation. The case of carbon disulfide, showing a solubility higher by a factor of 15 than expected from eq 5, has already baffled previous investigators[1,7] and no obvious explanation could be found.

In the case of sulfur hexafluoride the model is much more successful in accounting for the variance of the solubility data (see Figure 1b), and the small standard error, $\sigma = 0.15$ in log x_2, corresponds to discrepancies of 35% only in the solubilities themselves. No outlyers had to be kept away from the fit of all the available data.[3,16,17]

Figure 2 shows that the solubilities of C$_{60}$ and SF$_6$ in the same solvents are not correlated. The dissimilarity of eqs 5 and 7, describing the solubilities of C$_{60}$ and SF$_6$, respectively, is striking. The low-boiling sulfur hexafluoride is a very inert substance, similar to the inert gases in many respects, although somewhat larger (the diameter[3] of the largest, xenon, is 406 nm compared to 530 nm for SF$_6$). The depth of its potential well, $u/k = 205$ K, is in fact between those of Kr (189 K) and Xe (287 K).[3] Hence it is understandable that its solubility is governed (to ~82% of the variance) by the work needed to create the cavity for its accommodation, measured[11] by the surface tension of the solvents, eq 7 and Table 5. The polarity of the solvents, measured by the parameter $E_T(30)$, causes interactions with induced dipoles, SF$_6$ being fairly highly polarizable, $\alpha = 4.50 \times 10^{-30}$ m^3 molecule^{-1} (accounting for a further 6% of the variance). The solvent polarizability, measured by its molar refraction R, counteracts this and decreases the solubility. Thus the statistically derived eq 7 is readily rationalized in terms of the interactions that take place.

This is not the case for the solubility of C$_{60}$, where no single variable dominates the variance. It could be expected that due to the large size of this fullerene (a surface area $(1002/530)^2 = 3.6$ larger than that of SF$_6$), the work for the creation of the cavity for its accommodation would dominate its solubility. This work is related to the variables δ^2 or δ (the cohesive energy or its density), α (the hydrogen-bond-donation ability), γ (the surface tension), and $[C_p(l) - C_p(g)]/V$ (the structuredness) of the solvents, in various manners. However, none of these were required for the optimal fit, and their forced inclusion did not improve the fit of eq 5 to any extent. Although with a limited set of 15 solvents (at 303 K) comprising mainly hydrocarbons[7] the solubility of C$_{60}$ did yield a significant correlation in the form expected from eq 1 with the cohesive energy density δ

TABLE 6: Experimental and Calculated [Eq 7] Solubilities ($-\log x_2$) of SF$_6$ at 298 K in Various Solvents

| solvent	exptl	calcd	solvent	exptl	calcd
n-hexane	1.92	1.90	water	5.32	5.33
n-heptane	2.00	1.93	methanol	2.93	2.85
n-octane	2.02	1.95	ethanol	2.69	2.71
i-octane	1.81	2.05	*n*-octanol	2.49	2.56
n-decane	2.06	1.95	*n*-dodecanol	2.46	2.46
n-dodecane	1.92	2.02	1,2-ethanediol	4.30	3.96
n-tetradecane	1.91	1.87	1,4-dioxane	2.84	2.78
n-hexadecane	1.92	1.71	acetone	2.47	2.50
c-hexane	2.27	2.23	propylene carbonate	3.18	3.38
methyl-*c*-hexane	2.15	2.12	acetonitrile	2.85	2.89
benzene	2.58	2.48	benzonitrile	2.90	3.05
toluene	2.47	2.41	nitromethane	3.08	2.97
fluorobenzene	2.37	2.49	nitrobenzene	3.03	3.21
hexafluorobenzene	1.96	2.17	*N*-methylformamide	3.37	3.54
tetrachloromethane	2.55	2.68	*N,N*-dimethylformamide	3.11	3.03
chlorobenzene	2.18	2.34	*N,N*-dimethylacetamide	2.98	2.90
bromobenzene	2.70	2.78	*N*-methylpyrrolidinone	3.05	3.22
iodobenzene	2.91	2.87	hexamethyl phosphoramide	2.63	2.65
perfluoroheptane	1.65		carbon disulfide	3.03	2.65
perfluoro-Me-*c*-hexane	1.63		dimethyl sulfoxide	3.70	3.45
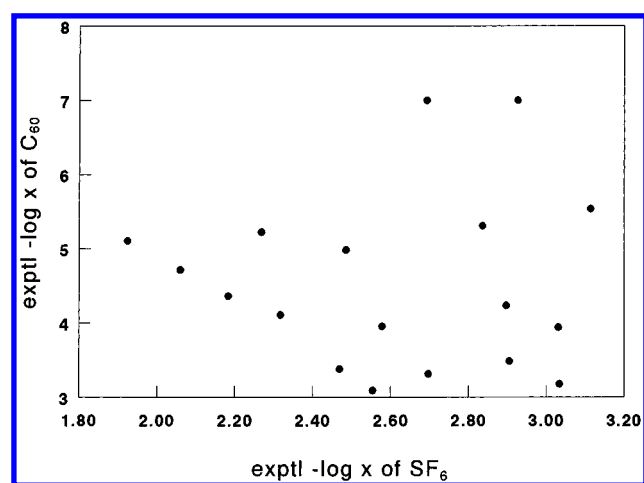
Figure 2. Comparison of the experimental solubilities ($-\log x_2$) at 298 K of C$_{60}$ fullerene and SF$_6$ for those solvents where data for both are available.

(except for CS$_2$), this was not at all the case for the more comprehensive set of solvents dealt with here (at both 298 and 303 K).

The very high polarizability[22] of C$_{60}$, $\alpha = 82.7 \times 10^{-30}$ m^3 molecule^{-1}, leads to the expectation that the polarity of the solvents would be a dominant factor in the solubility, but again this is contrary to the facts. The dipole moment of the solvents has a small negative effect on the solubility ($\sim$6% of the variance), the solubility in polar solvents being generally much lower than in nonpolar ones. The dominating effect in this respect is described in terms of the "general polarity" of the solvents, measured by $E_T(30)$ ($\sim$26% of the variance), rather than by the polarity function P (eq 2), perhaps because the latter involves the molar volume V, which may indirectly help the solubility (see below), although not included in the model. In fact, the solvent property measured by the function $P/V = (\epsilon - 1)/(\epsilon + 2)$ has been shown[1] for a limited set of solvents (but of all classes) to be detrimental to the solubility.

The polarizability of the solvents, measured by their molar refraction R and the polarity/polarizability parameter π^*, does, however, contribute positively to the solubility, accounting for $\sim$35 and $\sim$33% of the variance, respectively. The function $R/V = (n_D^2 - 1)/(n_D^2 + 2)$ has indeed been shown previously[1] to be conducive to high solubility. The role of π^* is more obscure, however. For the set of solvents treated here it is not correlated with R, although it has "polarizability" as an ingredient, and it is somewhat negatively correlated with μ and $E_T(30)$ (Table

2), which tend to decrease the solubility. One reason for its importance may be the relatively high values of π^* for aromatic solvents, which are capable of reacting with the spherical envelope of the 60 π-electron system of the fullerene.[2] Kamlet et al.[13] recommended modifying the $s\pi^*$ term in eq 4 by the inclusion of a decrement for aromatic solvents, to take this possibility into account. Since this decrement is the same for all aromatic solvents for a given solute, it can be incorporated in the XYZ$_0$ term of eq 4 or the constant terms in eqs 5 and 6, so that it need not be considered in the present context. The fusion of a second aromatic ring to the first one (1-methylnaphthalene compared with toluene or 1-iodonaphthalene compared with iodobenzene) tends to increase π^* somewhat,[23] but appears to have a larger effect on the solubility of C$_{60}$: a factor of 7–11.[1]

The size of the solvent molecules has not been required in the model for the solubility of C$_{60}$, although it could have been conceived to be important, either due to the number of such molecules that could interact with the π-electron system or due to the void space that can serve to accommodate the solute. The former reason appears not to be significant (π^* is a *bulk* property, not one of individual molecules) but the latter may have been incorporated in the R term, increased solvent volumes appearing to help the solubility. This is contrary to the supposition of Rouelle et al.[2] that C$_{60}$ accommodates more easily in small size solvent molecules (with respect to the partial molar volume), but in line with the presence of more void volume (with respect to the solubility). As found for the solvent compressibilities,[24] this void volume increases with the size of the solvent molecules and can be described[2,24] by the difference between the molar and intrinsic volumes of the solvents. On the other hand, the shape of the solvent molecules, whether predominantly oblate or prolate, does appear to have an effect. This shape can be estimated from the ratio of the van der Waals surface to the van der Waals volume of the molecules, those with the ratio < 13 nm^{-1} being oblate, the others prolate. The former, including aromatic solvents, appear to pack more efficiently around the C$_{60}$ sphere and generally permit enhanced solubilities.

In conclusion it is to be noted that whereas buckminsterfullerene, C$_{60}$, and sulfur hexafluoride, SF$_6$, are both large globular solutes, they have very different solubility characteristics. The former appears to have some direct interaction with certain solvents, via its envelope of π-electrons, whereas the latter is inert, due to the fluorine atoms surrounding it, and it resembles the inert gases (and fluorocarbons), as already

noted.[3-5] Still, the interaction that C$_{60}$ undergoes with solvent molecules is insufficient to confer on it high solubility, if physical characteristics of the solvent, such as available void volume, do not work in this direction. Thus, solvents with high polarizability and low polarity should be sought, as already noted by others.[1,7] Liquid polyphenyls come into mind in this respect (e.g., 1,3-terphenyl, T_m = 360 K).

References and Notes

(1) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379.

(2) Ruelle, P.; Farina-Cuendet, A.; Kesselring, U. V. *J. Am. Chem. Soc.* **1996**, *118*, 1777.

(3) Brückl, N.; Kim, J. I. *Z. Phys. Chem. (N. F.)* **1981**, *126*, 133.

(4) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1.

(5) Abraham, M. H.; *J. Am. Chem. Soc.* **1982**, *104*, 2085.

(6) Beck, M. T.; Mandi, G. *Fullerene Sci. Technol.* **1997**, *5*, 291.

(7) Sivaraman, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T. G.; Vasudeva Rao, P. R.; Mathews, C. K. *J. Org. Chem.* **1992**, *57*, 6077.

(8) Marcus, Y.; Kamlet, M. J.; Taft, R. W. *J. Phys. Chem.* **1988**, *92*, 3613. Marcus, Y. *Ibid.* **1991**, *95*, 8886. Marcus, Y.; Hefter, G. T.; Pang, T.-S. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1899.

(9) Hildebrand, J. H.; Scott, R. L. *Regular Solutions*, Prentice-Hall: Eglewood Cliffs, NJ, 1962; p 122.

(10) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

(11) Blander, M.; Grimes, W. R.; Smith, N. V.; Watson, G. M. *J. Phys. Chem.* **1959**, *63*, 1164.

(12) Marcus, Y. *J. Solution Chem.* **1996**, *25*, 455.

(13) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(14) Reichardt, Ch. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988.

(15) Marcus, Y. *J. Solution Chem.* **1991**, *20*, 929.

(16) Wilckock, R. J.; Battino, R.; Danforth, W. F.; Wilhelm, E. *J. Chem. Thermodyn.* **1978**, *10*, 817.

(17) Scharlin, P.; Battino, R. *J. Solution Chem.* **1992**, *21*, 67.

(18) Ruoff, R. S.; Malhotra, R.; Huestis, D. L.; Tse, D. S.; Lorents, D. C. *Nature* **1993**, *362*,140. Ruoff, R. S.; Olofsson, G.; Wadšo, I. In *Recent Advances in the Chemistry and Physics of Fullerenes*; Ruoff, R. S.;, Kadish, K. M., Eds., Electrochem. Soc.: Pennington, NJ, 1995; Vol. 3, p 1519.

(19) Smith, A. L.; Walter, E. In *Recent Advances in the Chemistry and Physics of Fullerenes*, Ruoff, R. S.; Kadish, K. M., Eds.; Electrochem. Soc.: Pennington, NJ, 1995; Vol. 3, p 1532.

(20) Zhou, X.; Liu, J.; Jin, Zh.; Wu, Y.; Gu, Zh. In *Recent Advances in the Chemistry and Physics of Fullerenes*; Ruoff, R. S., Kadish, K. M., Eds.; Electrochem. Soc.: Pennington, NJ, 1995; Vol. 3, p 1544.

(21) Korobov, M. V.; Gurvich, O. L. In *Recent Advances in the Chemistry and Physics of Fullerenes*; Ruoff, R. S., Kadish, K. M., Eds.; Electrochem. Soc.: Pennington, NJ, 1995; Vol. 3, p 1551.

(22) Quong, A. A.; Pederson, M. R. *Phys. Rev. B: Condens. Matter* **1992**, *46*, 12906.

(23) Ch. Laurence, Nicolet, P.; Dalati, M. T.; Abboud, J.-L. M.; Notario, R. *J. Phys. Chem.* **1994**, *98*, 5807.

(24) Marcus, Y.; Hefter, G. T. *J. Mol. Liq.* in press.