

ARTICLES

Solubility of C₆₀ Fullerene

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The most recent and comprehensive set of solubility data of C₆₀ fullerene in various solvents at 298 and 303 K was treated by multivariate stepwise linear regression applied as the linear solvation energy approach. In a few cases where the fullerene formed crystalline solvates, the enthalpy of incongruent melting and the temperature of maximum solubility were used to determine the “hypothetical solubility” of the unsolvated C₆₀, which was then used in the statistical procedure instead of the solubility of the solvate. The “ideal” solubility of the fullerene was estimated, and the “nonideal” part of the Gibbs energy of solution was then related to solute–solvent interactions. Increasing molar volume and solvent polarity (as measured by the Dimroth–Reichardt “general polarity” parameter, $E_T(30)$) diminished the solubility of C₆₀, whereas electron pair donation ability and polarizability enhanced solubility.

Introduction

Organic solvents have played an important role in the discovery of fullerenes and in investigations of their chemical properties. The Krätschmer–Huffman method of isolating C₆₀ works because this fullerene dissolves in benzene,¹ and virtually all of the synthetic reactions that functionalize fullerenes are carried out in organic solvents.²

The solubility of C₆₀ fullerene in organic solvents has previously been examined by one of us³ by means of the linear solvation energy (LSER) approach. According to this approach, the solvation energy, i.e., the interaction Gibbs energy of the solute with the solvent,⁴ depends in a linear manner on a small number of independently determinable physicochemical effects.⁵ A problem recorded there was the comparison of the solubilities of unsolvated C₆₀ with those of crystalline solvates, formed in several solvents. As more data have become available⁶ and the problem of the formation of crystalline solvates has found a solution by the use of “virtual” solubilities of the bare fullerene,^{6,7} a reexamination of the dependence of the solubility on the properties of the solvents became appropriate. These properties could either be measurable physical and chemical properties as used previously³ or ones computed by means of molecular mechanics⁸ or semiempirical quantum chemistry.⁹ Since the same statistical method, the LSER assumption, and measurable solvent properties as used previously were to be

applied, only data for solvents for which the required independent variables were known or could be reliably estimated could be employed. Hence, data for several solvents had to be left out from consideration. There remained 113 solubility data items for 298 K (Table 1) and 32 data items for 303 K (Table 2), which could be employed with as many independent variables (solvent properties) as were deemed pertinent. As before, subscript 1 pertains to the solvents and subscript 2 to the solute. Data in these tables come from a variety of published sources.^{10–17}

These solvent properties included the molar volume V_1 (at 298 K; $V_1(303\text{ K}) = V_1(298\text{ K})(1 + 5\alpha_{p1})$, where α_{p1} is the isobaric expansivity), the surface tension γ_1 , the solubility parameter δ_1 , the relative permittivity ϵ_1 , the dipole moment μ_1 , the square of the refractive index n_{D1}^2 , the Kamlet–Taft hydrogen bond donicity α_1 , electron pair donicity β_1 , and polarity/polarizability π^*_{11} , and the Dimroth–Reichardt “general polarity” parameter, $E_T(30)_1$ ¹⁸ (further described in the Discussion). Also included were the derived quantities δ_1^2 , $f(n)_1 = (n_{D1}^2 - 1)/(n_{D1}^2 + 2)$, the molar refraction $R_1 = V_1 f(n)_1$, $f(\epsilon)_1 = (\epsilon_1 - 1)/(\epsilon_1 + 2)$, the molar polarization $P_1 = V_1 f(\epsilon)_1$, and a function of the volume, $f(V)_1$, to be described later.

Effect of Solvates on Solubility

An aspect of the fullerene C₆₀ solubility that must be accounted for in any LSER analysis is that for some solvents the solid phase in equilibrium with the saturated fullerene solution at 298 K is not C₆₀ but its crystalline solvate. Significant decrease of solubility resulted from the formation of the C₆₀

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TABLE 1: Fullerene C₆₀ Solubility at 298 K^a

solvent	ref	log x_2	β	π^*	$E_T(30)$	R	V
<i>n</i> -pentane	8	-6.097	0.00	-0.15	31.1	25.5	116.1
<i>n</i> -hexane	8	-5.108	0.00	-0.11	31.0	29.9	131.6
2-methylpentane	9	-5.500	0.00	0.00	30.9	29.7	131.9
3-methylpentane	9	-5.343	0.00	0.00	30.9	29.6	129.7
<i>n</i> -heptane		-4.921	0.00	-0.06	31.1	34.8	147.5
<i>n</i> -octane		-4.658	0.00	0.01	31.1	39.4	163.5
<i>i</i> -octane	10	-5.194	0.00	0.01	31.1	38.9	160.4
<i>n</i> -nonane	10	-5.080	0.00	0.01	31.0	43.8	179.6
<i>n</i> -decane	8	-4.717	0.00	0.03	31.0	48.5	195.9
<i>n</i> -dodecane	10	-4.488	0.00	-0.01	31.1	57.8	228.6
<i>n</i> -tetradecane	10	-4.217	0.00	0.00	31.1	67.1	260.1
<i>c</i> -pentane	8	-6.523	0.00	0.00	30.9	23.1	94.7
<i>c</i> -hexane	8	-5.268	0.00	0.00	30.9	27.7	108.7
methyl- <i>c</i> -hexane	11	-4.510	0.00	0.04	30.7	32.5	128.4
ethyl- <i>c</i> -hexane	11	-4.310	0.00		30.9	37.1	142.5
<i>c</i> -hexene	11	-3.780	0.00	0.60	32.2	27.1	101.9
<i>cis</i> -decalin	8	-3.327	0.08	0.09	31.2	43.9	154.8
benzene		-3.161	0.10	0.55	34.3	26.4	89.9
toluene	8	-3.377	0.11	0.49	33.9	31.1	106.9
ethylbenzene	12	-3.435	0.12	0.53	34.1	31.9	123.1
<i>o</i> -xylene		-2.650	0.12	0.51	34.7	35.8	121.2
<i>m</i> -xylene		-3.119	0.12	0.47	34.6	36.0	123.4
<i>p</i> -xylene	13	-3.272	0.12	0.45	33.1	36.0	123.9
<i>n</i> -propylbenzene	13	-3.538	0.13		33.2	40.4	139.4
cumene	13	-3.635	0.18	0.41	34.6	40.5	140.2
1,2,3-trimethylbenzene	13	-3.057	0.13	0.45	32.9	40.5	134.4
1,2,4-trimethylbenzene		-1.976	0.13	0.45	32.9	40.0	134.4
mesitylene		-2.569	0.13	0.45	32.9	40.8	139.6
<i>n</i> -butylbenzene	13	-3.390	0.13	0.51	33.5	45.1	156.7
<i>sec</i> -butylbenzene	13	-3.620	0.13	0.51	33.5	45.0	156.4
<i>tert</i> -butylbenzene	13	-3.714	0.13	0.51	33.7	45.0	155.6
1,2,3,4- tetramethylbenzene	13	-2.920	0.14	0.45	33.0	44.9	149.0
1,2,3,5- tetramethylbenzene	13	-2.364	0.14	0.45	33.0	45.3	150.7
tetralin	8	-2.520	0.10	0.63	33.5	42.9	136.9
1-methylnaphthalene	8	-2.190	0.10	0.78	35.3	48.8	139.8
styrene	11	-3.220	0.12	0.57	34.8	36.6	115.6
fluorobenzene		-3.921	0.07	0.62	37.0	26.2	94.3
dichloromethane	8	-4.699	0.10	0.82	40.7	16.4	64.5
trichloromethane	8	-4.745	0.10	0.58	39.1	21.4	80.7
tetrachloromethane		-3.420	0.10	0.21	32.4	26.5	97.1
1,2-dichloroethane	12	-5.046	0.10	0.73	41.3	21.0	79.4
1,1,1-trichloroethane	12	-4.678	0.13	0.44	36.2	26.2	100.3
1,1,2,2-tetrachloroethane	8	-3.109	0.00	0.95	39.4	29.8	102.7
trichloroethene	8	-3.759	0.05	0.48	35.9	25.3	90.0
tetrachloroethene	8	-3.770	0.05	0.25	32.1	31.3	105.8
1-chloropropane	11	-5.523	0.00	0.43	37.4	20.8	88.9
1,2-dichloropropane	12	-4.854	0.10	0.70	42.1	25.7	98.3
1,3-dichloropropane	12	-4.820	0.10	0.60	40.2	25.7	95.8
1,2,3-trichloropropane	12	-3.939	0.10	0.78	40.4	30.3	106.6
chlorocyclohexane	12	-4.060	0.10		36.2	32.6	118.6
chlorobenzene		-2.991	0.07	0.68	36.8	31.2	102.2
<i>o</i> -dichlorobenzene		-2.162	0.03	0.77	38.0	36.0	113.1
<i>m</i> -dichlorobenzene		-2.889	0.03	0.65	36.7	36.1	114.6
1,2,4-trichlorobenzene	13	-2.745	0.00	0.66	36.2	41.0	124.8
benzyl chloride	12	-3.417	0.10	0.76	35.8	36.0	115.0
1-chloronaphthalene	8	-2.020	0.10	1.04	37.0	48.9	136.8
dibromomethane	12	-4.456	0.00	0.92	39.4	22.0	69.8
tribromomethane	11	-3.166	0.05	0.62	37.7	29.9	87.8
bromoethane	11	-5.150	0.18	0.53	32.5	19.1	75.1
1,2-dibromoethane	8	-4.222	0.00	0.75	38.3	27.0	86.6
1-bromopropane	12	-5.155	0.18	0.49	36.9	23.7	91.4
1-bromobutane	17	-3.747	0.18	0.47	36.6	28.3	108.0
bromo- <i>c</i> -hexane	12	-4.284	0.18	0.82	39.1	31.8	105.0
cyclohexyl bromide	12	-3.424	0.00		36.0	35.9	122.9
bromobenzene		-2.310	0.06	0.77	36.6	34.0	105.5
benzyl bromide	12	-3.089	0.10	0.85	35.5	38.7	118.9
iodomethane	12	-4.174	0.27		30.9	19.3	62.7
diiodomethane	12	-4.745	0.00	1.00	36.5	33.0	80.6
iodoethane	11	-4.509	0.27	0.65	30.7	24.3	81.1
1-iodopropane	12	-4.638	0.23	0.60	35.7	28.9	97.7
2-iodopropane	12	-4.770	0.19	0.73	30.7	29.3	100.3
iodobenzene		-1.523	0.05	0.84	36.2	39.2	111.9
bromochloromethane	11	-4.167	0.00	0.80	40.0	19.1	67.3
1,1,2-Cl ₃ -1,2,2-F ₃ -ethane	8	-5.699	0.00	0.01	33.2	26.2	119.8

TABLE 1 (Continued)

solvent	ref	log x_2	β	π^*	$E_T(30)$	R	V
methanol	9	-8.699	0.66	0.60	55.4	8.2	40.7
ethanol	9	-7.086	0.75	0.54	51.9	12.9	58.7
1-propanol	9	-6.398	0.90	0.52	50.7	17.6	75.1
2-propanol	9	-6.640	0.84	0.48	48.8	17.7	76.9
1-butanol	9	-5.921	0.84	0.47	49.7	22.2	92.0
2-butanol	9	-6.340	0.80	0.40	47.1	22.2	92.3
1-pentanol	9	-5.347	0.86	0.40	49.1	26.8	108.5
2-pentanol	9	-5.570	<i>0.80</i>	<i>0.40</i>	46.5	26.8	109.4
3-pentanol	9	-5.370	<i>0.80</i>	<i>0.40</i>	45.7	26.6	108.0
1-hexanol	9	-5.137	0.84	0.40	48.8	31.4	125.2
1-octanol	9	-4.987	0.81	0.40	48.1	40.7	158.4
<i>o</i> -cresol	8	-5.699	0.34	0.68	51.9	32.2	104.0
1,3-propanediol	9	-7.030	0.77	0.84	54.9	19.2	72.5
1,4-butanediol	9	-6.620	0.68	0.93	53.5	23.5	89.0
1,5-pentanediol	9	-6.190	0.82	0.76	51.9	28.3	105.6
tetrahydrofuran	8	-5.155	0.55	0.55	37.4	20.0	81.6
diglyme	12	-5.201	<i>0.41</i>	<i>0.64</i>	38.6	35.1	143.0
anisole	8	-3.073	0.32	0.70	37.1	32.9	109.3
benzaldehyde	12	-4.230	0.44	0.92	42.0	32.0	101.7
1-aminobutane	23	-3.296	0.72	0.31	37.6	24.0	99.3
aniline	15	-3.875	0.50	1.08	44.3	30.6	91.5
<i>N</i> -methylaniline	15	-3.755	0.47	0.82	42.5	35.7	109.1
<i>N,N</i> -dimethylaniline	15	-3.163	0.43	0.76	36.5	40.9	127.2
pyridine	8	-4.000	0.64	0.87	40.5	24.1	80.9
quinoline	13	-2.928	0.64	0.93	39.4	41.9	118.5
nitroethane	8	-6.699	0.15	0.77	43.6	17.0	71.9
nitrobenzene	8	-3.943	0.30	0.86	41.2	32.7	102.7
2-nitrotoluene	12	-3.400	<i>0.40</i>	<i>0.82</i>	40.8	37.2	117.9
3-nitrotoluene	12	-3.411	<i>0.40</i>	<i>0.82</i>	40.8	37.6	118.5
acrylonitrile	11	-6.440	0.25	0.87	46.7	15.6	66.2
benzonitrile	8	-4.237	0.37	0.88	41.5	31.6	103.1
dimethylformamide	12	-5.538	0.69	0.88	43.2	19.7	77.4
<i>N</i> -methylpyrrolidinone	8	-3.926	0.77	0.92	42.2	26.8	96.4
carbon disulfide	8	-3.180	0.07	0.51	32.8	21.4	60.6
thiophene	13	-4.360	<i>0.10</i>	<i>0.67</i>	35.4	24.4	79.5
2-methylthiophene	8	-3.040	<i>0.10</i>	<i>0.63</i>	34.7	29.3	96.8
tetrahydrothiophene	23	-4.854	0.44	0.60	36.8	26.2	88.7

^a Estimated values of the variables are in italics, and values of hypothetical solubilities, log x_2' , are in bold face.

TABLE 2: Fullerene C₆₀ Solubility at 303 K^a

solvent	ref	log x_2	β	π^*	$E_T(30)$	R	V
<i>n</i> -pentane	26	-6.187	0.00	-0.15	31.1	25.5	117.0
<i>n</i> -hexane	26	-5.133	0.00	-0.11	31.0	29.9	132.5
<i>n</i> -heptane	17	-4.209	0.00	-0.06	31.1	34.8	148.4
<i>n</i> -octane	26	-4.164	0.00	0.01	31.1	39.4	164.5
<i>i</i> -octane	17	-5.234	0.00	0.01	31.1	38.9	161.4
<i>n</i> -decane	26	-4.718	0.00	0.03	31.0	48.5	196.9
<i>n</i> -dodecane	26	-4.537	0.00	-0.01	31.1	57.8	229.7
<i>n</i> -tetradecane	26	-4.340	<i>0.00</i>	<i>0.03</i>	31.1	67.1	261.4
<i>c</i> -hexane	26	-5.114	0.00	0.00	30.9	36.9	109.4
benzene	26	-3.742	0.10	0.55	34.3	26.4	90.5
toluene	26	-3.451	0.11	0.49	33.9	31.1	107.5
<i>o</i> -xylene	26	-2.759	0.12	0.51	34.7	35.8	121.8
mesitylene	26	-3.827	0.13	0.45	32.9	40.8	140.3
tetralin	17	-2.523	0.10	0.63	33.5	42.9	137.4
dichloromethane	26	-4.640	0.10	0.82	40.7	16.4	64.9
tetrachloromethane	26	-4.060	0.10	0.21	32.4	26.5	97.7
<i>o</i> -dichlorobenzene	13	-2.912	0.03	0.77	38.0	36.0	113.6
1,2,4-trichlorobenzene	24	-3.039	0.00	0.66	36.2	41.0	125.3
<i>n</i> -bromobutane	17	-3.742	0.18	0.47	36.6	28.3	108.6
<i>n</i> -bromoheptane	17	-3.300	<i>0.00</i>	<i>0.41</i>	35.4	42.3	158.1
anisole	17	-2.991	0.32	0.70	37.1	32.9	109.8
<i>p</i> -bromoanisole	17	-2.551	<i>0.14</i>	<i>0.77</i>	37.5	37.8	120.5
dioxane	26	-5.309	0.37	0.49	36.0	21.7	86.2
tetrahydrofuran	17	-4.165	0.55	0.55	37.4	20.0	82.1
nitromethane	17	-4.822	0.15	0.75	46.3	12.5	54.3
pyridine	17	-4.470	0.64	0.87	40.5	24.1	81.3
2,4,6-trimethylpyridine	17	-2.792	0.78	0.66	36.4	38.9	133.7
piperidine	17	-2.129	1.04	0.50	35.5	26.7	100.1
pyrrolidine	17	-2.260	0.70	0.39	39.1	22.0	83.8
carbon disulfide	26	-3.359	0.07	0.51	32.8	21.4	61.0
thiophene	24	-4.538		0.67	35.4	24.6	79.9
tetrahydrothiophene	24	-4.810	0.44	0.60	36.8	26.2	89.1

^a Estimated values of the variables in italics.

TABLE 3: Thermodynamic Data for the Solid Solvates: Measured and Hypothetical Solubilities in the Systems C₆₀-C₆H₅F, -C₆H₅Cl, and -C₆H₅I

solvent	solvent composn C60:B	$\Delta_r H_2$, kJ/mol	T_{\max} , K	$10^4 x'$	$10^4 x$
C ₆ H ₅ F				1.2 ± 0.5	1.2 ± 0.5
C ₆ H ₅ Cl	1:2	18.2 ± 0.8 10.8 ± 1.1	301.2 ± 0.9 309.5 ± 0.7	11.4 ± 6.2	9.0 ± 0.9
C ₆ H ₅ I	1:2	50.2 ± 0.9	384.3 ± 0.5	300 ± 80	3.2 ± 0.5

solvates with aromatic solvents, with cyclohexane and CCl₄,^{6,7} and possibly with naphthalene derivatives. Other reported solvates with alkanes (with the exception of octane) and haloalkanes appear to affect solubility to a lesser extent. To discuss solubilities in terms of solvent properties, it is necessary to separate out the impact of solvates and to compare saturated concentrations relative to one and the same solid phase, unsolvated C₆₀, even though in some systems the unsolvated phase is metastable at room temperature.

For solvents which make stable room-temperature solvates with C₆₀, it is possible^{6,7} to calculate a hypothetical solubility, x_2' , of the unsolvated C₆₀ in terms of the measured solubility, x_2 :

$$\ln(x_2') = (\Delta_r H_2 / RT) (1 - T/T_{\max}) + \ln(x_2) \quad (1)$$

Here $\Delta_r H_2$ is the enthalpy of incongruent melting or decomposition of the solvate and T_{\max} is the incongruent melting (IM) temperature of the solvate ($T_{\max} > 298$ K). To derive eq 1 it was assumed that $\Delta_r H_2$ is temperature-independent in the temperature range from 298 to T_{\max} . If two solvates are formed in the system, two similar terms with different $\Delta_r H_2$ and T_{\max} must be included in the right-hand side of eq 1.

The first term in the right-hand side of eq 1 corrects for the impact of the stability of a solid solvate. It is the quantity $\ln(x_2')$ (or, in this paper, $\log(x_2')$) which should be used to correlate with the solvent properties. Additional determinations of $\Delta_r H_2$, T_{\max} , and $\log(x_2')$ were made for three solvents as a part of the present work using differential scanning calorimetry (DSC). Alternatively, but with the need for considerably more experimental work, $\ln(x_2')$ could be obtained from the heat of solution of the fullerene $\Delta_{\text{sol}} H_2$ below T_{\max} , obtained calorimetrically, and the quantity $T(d(\ln x_2)/dT)$, obtained from the slope of the solubility curve above T_{\max} :

$$\ln(x_2'/x_2) = [T(d(\ln x_2)/dT) - \Delta_{\text{sol}} H_2 / RT](1 - T/T_{\max}) \quad (2)$$

The hypothetical solubilities, x_2' , of the unsolvated C₆₀ may be from 1.2 to 100 times higher than the observed solubilities of the solvates, x_2 .

Determination of Solvate Parameters

In the present work DSC was used to identify solid solvates and to determine $\Delta_r H_2$ and T_{\max} in the binary systems C₆₀/C₆H₅F, C₆₀/C₆H₅Cl, and C₆₀/C₆H₅I. Measurements were carried out with a DSC-30 Mettler instrument. The experimental procedure was described in detail elsewhere.⁷ The results of measurements performed in the systems mentioned above are presented in Table 3. As it is seen from the table, fluorobenzene does not form solvates with C₆₀. The solvate of C₆₀ with C₆H₅Cl (1:2) undergoes two-step decomposition. Formation of the solid solvate of C₆₀ with iodobenzene lowers the solubility of C₆₀ approximately by a factor of 100. This latter example demonstrates how crucial the effect of solvates on solubility can be.

In Table 4 are gathered the hypothetical solubilities, incon-

TABLE 4: Hypothetical Solubilities and Temperatures T' of the Incongruent Melting (IM) for the Systems of C₆₀ with Mostly Aromatic Solvents

solvent	T' (IM), K	equilibrium solid phase at $T = 298$ K	$10^4 x'$	$10^4 x$
C ₆ H ₆	(322)	C60·4C ₆ H ₆	(6.9)	2.0
C ₇ H ₈	284 (285)	C60·2C ₇ H ₈	4.2 (4.2)	4.2
C ₆ H ₅ Cl	301 (306) 309 (331)	C60·2C ₆ H ₅ Cl	11.4 ± 6.2 (16.9)	9.0
C ₆ H ₅ Br	347 (350)	C60·2C ₆ H ₅ Br	48.8 (54.6)	4.4
C ₆ H ₅ I	384 (389)	C60·2C ₆ H ₅ I	300 ± 80 (370)	3.2
1,2-C ₈ H ₁₀	310 (322)	C60·2C ₈ H ₁₀	24.0 (37.7)	14.7
1,3-C ₈ H ₁₀	362 (370)	C60·0.6C ₈ H ₁₀	9.6 (10.4)	3.6
1,2-C ₆ H ₄ Cl ₂	322 (325)	C60·2C ₆ H ₄ Cl ₂ ^a	67.6 (71.2)	38.3
1,3-C ₆ H ₄ Cl ₂	394 (406)	C60·0.6C ₆ H ₄ Cl ₂	12.7 (19.7)	3.8
1,3,5-C ₉ H ₁₂	429 (460.8)	C60·0.5C ₉ H ₁₂	24.6 (41.6)	3.3
1,2,4-C ₉ H ₁₂	(322)	C60·2C ₉ H ₁₂	(105.7)	33.5
C ₈ H ₁₈	398	C60·C ₈ H ₁₈	0.22	0.045
CCl ₄	(319) 388 (402)	C60·13CCl ₄	3.8 (4.2)	0.43

^a This solvate exists in two polymorphic modifications, with the incongruent melting temperatures 322 and 342 K, respectively.⁵ It was believed that the former solvate was an equilibrium solid phase in the course of solubility measurements.

gruent melting temperatures, and equilibrium solid phases at 298 K for C₆₀ with mostly aromatic solvents.

Estimation of the Accuracy of the Hypothetical Solubilities

Before establishment of correlations between hypothetical solubilities, x' , and the solvent properties, the reliability of existing data on x' must be assessed. As it is seen from eq 1, the hypothetical solubility is determined by the enthalpy, $\Delta_r H_2$, and by the incongruent melting temperature, T_{\max} . The enthalpies measured were independent of the experimental conditions (see Table 1 of ref 7). DSC gave two reproducible estimates of the equilibrium incongruent melting temperature. Numbers in column 2 of Table 4 are onset temperatures of the DSC peaks measured in the present study, while numbers in brackets are temperatures of peak maximums. Equilibrium incongruent melting temperature can be 5–15 deg below the temperature of the DSC peak maximum; i.e., onset temperatures probably give better estimates of T_{\max} . The last-mentioned statement was proved in an additional DSC experiment with Na₂SO₄·10H₂O, where the measured onset temperature was close to the literature value of the incongruent melting temperature, 305.7 ± 0.5 and 305.5 K, respectively. For the systems under study the onset temperatures were shown to be independent of the scanning rate in the DSC experiment. As a result, it was decided to use for correlations with the solvent properties the values of x' based on the onset temperatures, (numbers in column 4 of Table 4), rather than those based on the temperatures of maximum (numbers in brackets in column 4 of Table 4). The difference in the two numbers in column 4, however, is within the limits of the experimental error of solubility measurements. In many cases it is much less than the difference between x' and x .

Multivariate Statistical Analysis

The stepwise linear regression statistical method (Crunch v. 4.0) employed previously was used again. The standard molar Gibbs energy of solution, to which the LSER assumption pertains, is $\Delta_{\text{soln}} G_2 = -RT \ln x_2$, where x_2 is the equilibrium mole fraction of the solute, C₆₀, in the saturated solution at the temperature T . In the following, $\log_{10} x_2$ is used instead of $\Delta_{\text{soln}} G_2$, in view of previous usage.

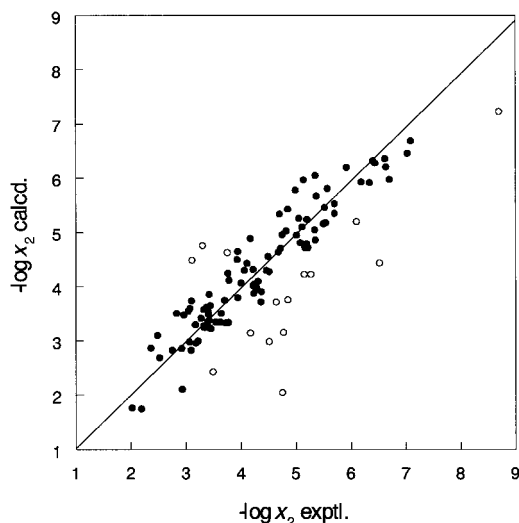


Figure 1. Solubility of C₆₀ in various solvents at 298 K: 113 solvents included in the correlation (eq 3); 18 outlying solvents excluded from the correlation.

For the data at 298 K the best correlation that could be arrived at was with an adjusted multiple correlation coefficient squared,

$$\log x_2 \text{ (or } x_2', \text{ where appropriate)} = (-0.1298 \pm 0.0040)E_T(30)_1 + (0.2264 \pm 0.0109)R_1 + (-0.0592 \pm 0.0031)V_1 + (0.729 \pm 0.197)\beta_1 \quad (3)$$

$R_{\text{corr}}^2 = 0.9915$ (i.e., 99% of the variance of the data was "explained" by the independent variables of the correlation) and a standard error of $\sigma = 0.411$ in $\log x_2$. This correlation pertained to 95 out of the 113 items, with $F_{4,91} = 2781$ as the relevant statistic, leaving 18 outliers with deviations $>2\sigma$ not included in the correlation. According to the F -to-remove from the correlation statistic, the variable $E_T(30)_1$ accounted for 56% of the variance, R_1 for 24%, V_1 for 20%, and β_1 for 9%. The ratios of the coefficients of these variables to their standard errors are another indication of their relative contributions. The results of correlation (3) are shown in Figure 1.

The outliers were *n*-pentane (+0.98), *c*-pentane (+2.15), *c*-hexane (+1.13), ethylbenzene (−0.95), 1,2,4-trimethylbenzene (+1.12), 1,1,2,2-tetrachloroethane (−1.32), 1,2-dichlorobenzene (−1.27), bromoethane (+0.96), bromobutane (−0.84), iodomethane (+1.04), diiodomethane (+2.73), iodoethane (+1.44), 1-iodopropane (+0.95), 2-iodopropane (+1.64), iodobenzene (+1.10), methanol (+1.48), 1-aminobutane (−1.48), and tetrahydrothiophene (+1.10). In parentheses are the deviations: the calculated $\log x_2$ minus the experimental value. The preponderance of the iodoalkanes among these outliers is noteworthy—in fact, none of the iodoalkanes for which data were available fit the correlation (3). Their deviations are all positive: $(1.27 \pm 0.22)n_i$, where n_i is the number of iodine atoms in the solvent molecule. This might be indicative of either poor estimates of the values of one of the variables [probably $E_T(30)_1$] or the occurrence of a specific interaction of the fullerene with the iodine atom of the solvent. The outlying cases of *n*-pentane, *c*-pentane, and methanol might be due to the extremely low solubilities of the fullerene in these solvents, being given to only one significant figure, hence not being determined accurately and possibly being underestimated. On the other hand, the solubility of the fullerene in 1-aminobutane was much higher than was accounted for by correlation (3) and could be due to a specific interaction of this basic solvent not describable by

the variable β_1 . (See below for the cases of piperidine and pyrrolidine for the solubility at 303 K.) Positive deviations for 1,2-dichlorobenzene, 1,2,4-trimethylbenzene, iodobenzene, and *c*-hexane could be due to the formation of solvates in these systems. This left the outliers ethylbenzene, 1,1,2,2-tetrachloroethane, bromoethane, and tetrahydrothiophene with no explanation of their deviations.

Correlation (3) was also tried for the data at 303 K, but the results were less satisfactory, since the list of solvents was much shorter and the overall variations in their properties were smaller:

$$\log x_2 = (-0.1085 \pm 0.0081)E_T(30)_1 + (0.1836 \pm 0.0272)R_1 + (-0.0512 \pm 0.0068)V_1 + (1.501 \pm 0.403)\beta_1 \quad (4)$$

Here $R_{\text{corr}}^2 = 0.9840$ (i.e., 98% of the data variance "explained") and $\sigma = 0.483$, pertaining to 25 out of the 32 items, with $F_{4,21} = 386$, leaving 7 outliers with deviations $>2\sigma$. These were *n*-pentane (+1.50), *c*-hexane (+2.94), dioxane (+1.53), pyridine (+1.30), pyrrolidine (−1.18), thiophene (+1.27), and tetrahydrothiophene (+1.73). A better correlation of the 303 K data was obtained when the polarizability R and the electron pair donicity β_1 were replaced by the polarity/polarizability parameter π^* . With only three variables the results were

$$\log x_2 = (-0.1781 \pm 0.0099)E_T(30)_1 + (-0.0049 \pm 0.0018)V_1 + (4.35 \pm 0.35)\pi^*_1 \quad (5)$$

with $R_{\text{corr}}^2 = 0.9907$ (i.e., 99% of the data variance "explained") and $\sigma = 0.388$, pertaining to 25 out of the 32 items, with $F_{3,22} = 886$, leaving again 7 outliers with deviations $>2\sigma$. These were dichloromethane (+1.28), dioxane (+1.46), pyridine (+1.45), pyrrolidine (−2.16), piperidine (−1.51), thiophene (+1.55), and tetrahydrothiophene (+1.31).

Another possibility was to ignore the temperature difference and add the 303 K data to those at 298 K. In fact, some of the data nominally reported in compilations under the heading 298 K were actually obtained at room temperatures that varied between 293 and 298 K during the equilibrations.¹⁰ If the same solvent was represented at the two temperatures, either the two entries or their mean could be used or one of the two values could be preferred. In some such cases there was a large difference in the solubilities at the two temperatures (e.g.,⁶ nitromethane, $x_2(298) = 0.000 \times 10^{-4}$, $x_2(303) = 0.15 \times 10^{-4}$, and tetrahydrofuran, $x_2(298) = 0.07 \times 10^{-4}$, $x_2(303) = 0.6 \times 10^{-4}$) whereas in others the values were very near (e.g.,⁶ tetralin, $x_2(298) = 30.1 \times 10^{-4}$, $x_2(303) = 29.7 \times 10^{-4}$, and dichloromethane, $x_2(298) = x_2(303) = 0.23 \times 10^{-4}$). When all the data items were used, the correlation (3) was still applicable with very minor changes (but a somewhat larger standard error):

$$\log x_2 \text{ (or } x_2', \text{ where appropriate)} = (-0.1294 \pm 0.0036)E_T(30)_1 + (0.2197 \pm 0.0099)R_1 + (-0.0573 \pm 0.0027)V_1 + (0.758 \pm 0.183)\beta_1 \quad (6)$$

Here $R_{\text{corr}}^2 = 0.9909$ (i.e., 99% of the data variance "explained") and $\sigma = 0.418$, pertaining to 120 out of the 145 items, with $F_{4,116} = 3268$, leaving 25 outliers with deviations $>2\sigma$. These were essentially the same as those outlying in the separate temperature correlations (*n*-pentane, *c*-hexane, and tetrahydrothiophene appearing twice).

It should be noted that in addition to the 145 solvents considered in the correlations, 24 solvents for which solubilities have been measured had to be excluded from consideration

because the relevant parameters [$E_T(30)$ and β] were unknown or could not be reliably estimated. These were phenyl isocyanate, 1-phenylnaphthalene, 1-bromo-2-methylnaphthalene, 1-methyl-1-cyclohexene, thiophenol, 1,2-dimethylcyclohexane, mixed *cis*- and *trans*-decalin, *trans*-decalin, dichlorodifluoroethane, 1,3-dibromo- and diiodopropane, 1,2,3-tribromopropane, 1- and 2-chloro-, bromo-, and iodo-2-methylpropane, cyclopentyl bromide, and cyclohexyl iodide,⁶ as well as 1-bromotetradecane and -octadecane, diglyme, 3-bromoanisole, and 1-tetralone.¹⁹ Data for water, acetone, nitromethane, acetonitrile, and hexamethylphosphoramide, for which the mole fraction solubility was $<1 \times 10^{-9}$, could not be used either.

Discussion

A major difference of the present correlations (3)–(6) compared to those in the previous report³ is the absence of a constant in the regressions. The statistical program rejected emphatically the need for such a constant (the F statistic for its inclusion being <1). On the other hand, the standard error for the present database, which contains twice as many solvents as the previous one, is about the same (slightly larger) but the “explaining power” of the regression (R_{corr}^2) is considerably larger than before: 0.9915 for correlation (3) compared to 0.8590 previously. The inclusion of V and β now rather than π^* previously is less important as the comparison of the correlations (4) and (5) (for the 303 K data) shows. Furthermore, for the entire set of solvents π^*_1 is fairly well correlated with V_1 ($R_{\text{corr}} = 0.8457$). The inclusion now of an additional variable, β_1 (instead of μ_1 employed previously³), though contributing much less to “explaining” the variance, is justified in view of the large “covalent hydrogen bonding acidity” attributed⁹ to C_{60} .

However, the question of the justification of the inclusion of a constant in the correlations should perhaps not be left to the statistical program. When the solubility of solid (C_{60}) in liquid solvents is to be explained, the possible interactions which are explained by the properties of the solvents^{3,8} should be dealt with after the “ideal solubility” is determined, i.e., that solubility that reflects the entropy change of dispersing the solute in the solution without its interactions with the solvent.^{20,21} For this purpose the solid C_{60} is first permitted to “fuse” at $T = 298$ K into a “supercooled liquid” that is then dissolved in the solvent. This involves the entropy of fusion $\Delta_{\text{fus}}S_2 = \Delta_{\text{fus}}H_2/T_{\text{fus}2}$ and that resulting from the temperature change from that of fusion, $T_{\text{fus}2}$, to $T = 298$ K and can be expressed as^{20,21}

$$\ln x_2(\text{ideal}) = [-(\Delta_{\text{fus}}H_2/RT_{\text{fus}2}) + (\Delta C_{P2}/R)] \times [(T_{\text{fus}} - T)/T] + (\Delta C_{P2}/R) \ln(T/T_{\text{fus}2}) \quad (7)$$

where, as before, subscript 2 refers to the fullerene, $\Delta_{\text{fus}}H_2$ is the enthalpy of fusion, and $\Delta C_{P2} = C_{P2}(C_{60,l}) - C_{P2}(C_{60,c})$ is the difference in heat capacity between the “supercooled liquid” and the crystalline fullerene. Since, however, $C_{P2}(C_{60,l})$ is unknown, the temperature independence of ΔC_{P2} , assumed in eq 7, is immaterial and the approximation $\Delta C_{P2}T_{\text{fus}2} \approx \Delta_{\text{fus}}H_2$ has to be used,²⁰ producing

$$\ln x_2(\text{ideal}) = (\Delta_{\text{fus}}H_2/RT_{\text{fus}2}) \ln(T/T_{\text{fus}2}) \quad (8)$$

Solute–solute interactions²² need not be taken into account in this derivation due to the very low molar solubilities encountered.

The expression (8) does not depend on the solvent but describes properties of the fullerene itself and can, in principle, be evaluated independently. The fullerene C_{60} has not been so

far observed to fuse at any temperature, but some estimates of $T_{\text{fus}2}$ have been reported: >950 K;²³ ≥ 1200 K;²⁴ 2023 K.^{25,26} The enthalpy of fusion $\Delta_{\text{fus}}H_2$ was obtained from the measured enthalpy of sublimation of the solid and an estimated enthalpy of vaporization of the liquid fullerene: $\Delta_{\text{fus}}H_2 = \Delta_{\text{subl}}H_2 - \Delta_{\text{vap}}H_2$. The enthalpy of sublimation $\Delta_{\text{subl}}H_2$ at ambient temperature was given as 173.2 ,¹⁰ 181 ,²⁴ and as 182 ± 3 27 kJ mol^{-1} . The enthalpy of vaporization can be obtained from the solubility parameter δ_2 ascribed to the fullerene: $\Delta_{\text{vap}}H_2 = RT + V_2\delta_2^2$. The value of δ_2 of the fullerene, in turn, is estimated from matching the maximum in a plot of its solubilities in nonpolar solvents against their solubility parameters, δ_1 . This, in a way, can be construed as circular reasoning, but it does not compromise the entire database used for the correlations. Such estimates of $\delta_2/\text{MPa}^{1/2}$ are 20.0 ¹⁶ (actually, obtained from substituting $\Delta_{\text{subl}}H_2$ for $\Delta_{\text{vap}}H_2$, but this δ_2 matches well the above-mentioned maximum), 18.8 or 19.2 ,¹⁶ and 18.5 .¹⁷ The latter three values lead to $\Delta_{\text{vap}}H_2$ between 166.8 and 179.4 kJ mol^{-1} , taking $V_2 = 480$ $\text{cm}^3 \text{mol}^{-1}$, according to Ruelle et al.²⁹ The difference $\Delta_{\text{fus}}H_2 = \Delta_{\text{subl}}H_2 - \Delta_{\text{vap}}H_2$ is then ≤ 15 kJ mol^{-1} , depending on the choice of the values of $\Delta_{\text{subl}}H_2$ and $\Delta_{\text{vap}}H_2$. Other estimates of $\Delta_{\text{fus}}H_2$ are 20 – 30 ²⁸ and ≈ 12 24 kJ mol^{-1} . Two contradictory estimates of $\Delta_{\text{fus}}H_2$ appear on the same page in a publication,²⁶ neither of which making sense: “ $\Delta H_{\text{ml}} \dots$ enthalpy of fusion $\dots = 74.8$ kJ mol^{-1} ” and “the enthalpy of melting ΔH_{ml} , was found to be 2493 kJ mol^{-1} ”. The resulting best estimate of the entropy of fusion $\Delta_{\text{fus}}S_2 = \Delta_{\text{fus}}H_2/T_{\text{fus}2}$ with $12 \leq \Delta_{\text{fus}}H_2 \leq 15$ kJ mol^{-1} , and the estimated $T_{\text{fus}2} \sim 1200$ K is 11 ± 2 $\text{J K}^{-1} \text{mol}^{-1}$. The heat capacity at constant pressure of the crystalline C_{60} fullerene was reported²³ as $C_{P2}(C_{60,c}) = 536.9$ $\text{J K}^{-1} \text{mol}^{-1}$ at ambient temperatures. Due to the spherical nature of the fullerene, it could be a good approximation to assume that the heat capacity of the (supercooled) liquid is larger by the translational contribution $1.5R$ only, excited by the fusion. Thus $\Delta C_{P2}T_{\text{fus}2}$ becomes 15 kJ mol^{-1} and is well compatible with (the assumed upper limit of) $\Delta_{\text{fus}}H_2$ to make the assumption $\ln x_2(\text{ideal}) = (\Delta_{\text{fus}}H_2/RT_{\text{fus}2}) \ln(T/T_{\text{fus}2})$, eq 8, plausible. The value $\log x_2(\text{ideal}) = -4.34 \pm 0.43$ results from eq 8. An aspect of the $E_T(30)_1$ variable in eq 3 or 6 to be noted is that it has a finite value for completely nonpolar solvents, 30.9 (the units are kcal mol^{-1}), the values of polar solvents extending above this up to 63.1 for water. Thus, both eqs 3 and 6 have a “built-in constant” of -3.96 ± 0.14 , corresponding fairly well to that required by the “ideal” solubility estimated above as -4.34 ± 0.43 in $\log x_2$.

A further fact that has to be allowed for, and which is partly solvent-independent and could be included in a constant of the correlation, is the disparity in the molar volumes of the solute and solvents. An appropriate expression can be borrowed from the Flory athermal mixing approach:³⁰

$$\ln x_2(\text{volume}) = \ln(V_1/V_2) + (V_2 - V_1)/V_1 = [-\ln(V_2/V^\circ) - 1] + \ln(V_1/V^\circ) + V_2/V_1 \quad (9)$$

Here subscript 1 pertains to the solvent, $V^\circ = 1$ $\text{cm}^3 \text{mol}^{-1}$, and V_2 is the molar volume of the “supercooled liquid” fullerene. The term in brackets in the second equality of eq 9 is again solvent-independent and could be added to the ideal solubility to yield the constant in the correlation. When the estimate of Ruelle et al.²⁹ for V_2 of the “supercooled liquid” fullerene, 480 $\text{cm}^3 \text{mol}^{-1}$, is borrowed again, the term in brackets of eq 9, converted to decadic logarithms, becomes -3.12 . The remaining quantity in eq 9 is designated as $f(V_1) = \log(V_1/V^\circ) + (V_2/V_1)/\ln 10$.

TABLE 5: Prediction of the Very Low Solubilities of C₆₀ in Solvents at 298.15 K

solvent	$E_T(30)_1$	R_1	V_1	β_1	$\log x_2$	predicted solubility	
						$\mu\text{mol dm}^{-3}$	$\mu\text{g mL}^{-1}$
water	63.1	3.7	18.1	0.47	-8.0	0.6	0.4
methanol	55.4	8.2	40.7	0.66	-7.2	1.5	1.1
1,2-ethanediol	56.3	14.5	55.9	0.52	-6.9	2.1	1.5
glycerol	57.0	20.5	73.2	0.51	-6.7	2.9	2.1
acetone	42.2	16.2	74.0	0.48	-5.8	20	15
acetonitrile	45.6	11.1	52.9	0.40	-6.2	12	8
nitromethane	46.3	12.5	54.0	0.06	-6.2	11	8

The correlation of the left-hand side of eq 6 with the solvent properties should, therefore, be made to take care also of the “ideal” solubility of the fullerene and the volume effect. The volume effect could, perhaps, be taken into account by $f(V_1)$ rather than by the term in $-V_1$ as in eq 6. This was tried but with quite poor results (standard error $\sigma = 0.882$), since both variables were needed, yielding

$$\log x_2 + 4.34 + 3.12 = (-0.0772 \pm 0.0096)E_T(30) + (0.2414 \pm 0.0124)R + (-0.0487 \pm 0.0034)V + (0.985 \pm 0.090)f(V) \quad (10)$$

with $R_{\text{corr}}^2 = 0.9760$ (i.e., ~98% of the data variance “explained”) and $\sigma = 0.531$, pertaining to 120 out of the 145 items, with $F_{4,116} = 1219$. Although the “explaining power” with the added variable $f(V)$ in eq 10 is not much worse than that of eq 6, the standard error is appreciably larger, as is also reflected by the smaller value of the F statistic. The coefficients of the terms in R and V are, within the limits of error, the same as before, but β is not required anymore. As regards the F -to-remove criterion, the terms in R and V are now the dominant ones (compared with that in $E_T(30)$ in eqs 3–6), with that in $f(V)$ contributing less. Interestingly, the use of $f(V)$ in the correlation does not preclude that of V , but on the contrary, requires it emphatically from the statistical viewpoint. No other variables were accepted by the statistical program for this correlation. This means that the Flory approximation, eq 9, well applicable to multisegmented chainlike molecules in unisegment solvents, is not particularly successful with a globular solute, such as the fullerene C₆₀.

The rationalization of the correlations of the solubility of the fullerene with $E_T(30)_1$ and R_1 , presented previously,¹ is obviously justified also for the more extensive data set now employed. The $E_T(30)_1$ parameter of Dimroth and Reichardt¹⁸ is based on the solvatochromic shift of a betaine, a highly polarizable polyaromatic dye with an exposed negatively charged oxygen atom, and it describes the “general polarity” of the solvent. This depends to a major degree on the hydrogen bond donation ability in the case of protic solvents (corresponding to the Kamlet–Taft α_1) but also on the solvent polarity/polarizability (measured by the Kamlet–Taft π^*_1).³¹ An aspect of the effect of $E_T(30)_1$ that was not noted previously is that this variable is high for the more structured solvents.³² Its negative effect might be related to this, but it is still puzzling that the large amount of work required for the creation of the cavity in the solvent, needed to accommodate the large C₆₀ fullerene molecules, is not reflected by a term related to the solvent cohesive energy in the correlation expressions (the δ_1 and δ_1^2 variables were definitely rejected by the statistical program). The negative effect of increasing solvent molar volume V_1 may be related to the diminishing number of solvent molecules that surround the fullerene molecule, hence the lower direct solvation interactions. Note also that in eq 9 V_1 of the

major term on the right-hand side is in the denominator, so that this term becomes less positive (decreasing the solubility) as V_1 increases. The positive, though small, effect of the Lewis basicity of the solvent, expressed by β_1 , in view of the large “covalent hydrogen bonding acidity” attributed⁹ to C₆₀, has already been commented on above. The sizable “covalent hydrogen bonding basicity” also attributed by these authors to the fullerene should be conducive to the solubility in solvents with high α_1 , the hydrogen bond donation ability of the solvents. But α_1 has nonzero values for only a few of the solvents considered, so that its positive effect is obscured by the negative effect of their large structuredness; see above.

With a workable correlation expression, such as eq 6, it is possible to predict the solubility of the C₆₀ fullerene in solvents in which it is so low that it could not so far be determined reliably.^{6,17} Table 5 contains some such predictions for 298.15 K. As expected,¹¹ the predicted solubility in water is very low indeed but not as low as it appears to be in the recent paper by Abraham et al.³³ Both the solubility in water and the vapor pressure of C₆₀ at 298.15 are extremely low and not measurable with present day facilities. Hence, it is questionable whether such quantities should be taken as reference states with which the solubilities in hydrocarbons and alcohols should be compared,³³ in order to extract the relevant solute properties (excess molar refractivity, dipolarity/polarizability, hydrogen bond basicity, and gas–liquid partition coefficient on hexadecane) that are not measurable either. Since 5 coefficients have to be determined for each solvent from partition data of many solutes (for statistical validity), the prediction of the solubility of C₆₀ in solvents other than those already treated by the LSER expressions presented³³ would involve an incommensurate effort. The present approach permits predictions of solubilities within 1 order of magnitude (2σ of the correlations) with much less effort.

Conclusion

In this paper we have subjected the most recent and comprehensive set of solubility data of C₆₀ fullerene in various solvents at 298 and 303 K to multivariate stepwise linear regression applied as the linear solvation energy approach. For aromatic solvents where the fullerene formed crystalline solvates, the enthalpy of incongruent melting and the temperature of maximum solubility were used to determine the “hypothetical solubility” of the unsolvated C₆₀, which was then used in the statistical procedure instead of the solubility of the solvate. The “ideal” solubility of the fullerene was estimated, and the “nonideal” part of the Gibbs energy of solution was then related to solute–solvent interactions. For the correlations of eqs 3 and 6, adjusted multiple correlation coefficients R_{corr}^2 of >0.99 were achieved after removing outliers. Increasing molar volume and solvent polarity (as measured by the Dimroth–Reichardt “general polarity” parameter, $E_T(30)$) diminished the solubility

of C₆₀, whereas electron pair donation ability and polarizability enhanced solubility.

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