Solubility of C_{60} in a Variety of Solvents

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The room temperature solubility of pure C_{60} has been determined in 47 solvents. The solubilities cover a wide range, from 0.01 mg/mL in methanol to 50 mg/mL in 1-chloronaphthalene. The solubilities in CS_2, toluene, and hexane, three of the commonly employed solvents, are 7.9, 2.8, and 0.04 mg/mL, respectively. An examination of the solubilities of C_{60} as a function of the solvent properties such as index of refraction, dielectric constant, molecular size, Hildebrand solubility parameter, and H-bonding strength reaffirms the century-old principle "like dissolves like". No single solvent parameter can uniformly predict the solubility of C_{60}, but a composite picture of solvents with high solubility for C_{60} emerges: large index of refraction, dielectric constant around 4, large molecular volume, Hildebrand solubility parameter equal to 10 $cal^{1/2}$ $cm^{-3/2}$, and tendency to act as a moderate strength nucleophile.

Introduction

The solubility of C_{60} and other fullerenes is of both practical and fundamental interest. Extraction and purification of solutes by solvents are significant and costly processes in the production of chemicals and can constitute on the order of 50% of the overall cost of production.[1] Extraction and chromatographic techniques currently employed for the isolation of C_{60},[2-5] and of other pure fullerenes, are much too expensive to allow large scale production and utilization by the chemical industry. A deeper understanding of the interaction of fullerenes with various solvents will allow rational choice of solvents capable of purifying the fullerenes by cheaper and scalable methods. Solubility data can also play a useful role in the choice of stationary phase and type of chromatography employed.

The fullerenes, with their unique cage structures, will interact with solvents in interesting ways that provide new information on the mechanisms of solute–solvent interactions. The fullerenes have rigid, well-defined geometries, in contrast to other solutes whose shapes undergo conformational changes and whose intramolecular vibrational partition functions may undergo large—and solvent dependent—changes. A zero-order picture of the interaction afforded by a fullerene solute with a solvent would include two aspects of the geometry of the fullerene: the molecular surface area and the molecular volume. The molecular volume is the volume of the cavity created in the solvent liquid, and the molecular surface area is the surface available for interaction with the solvent. Adams and Ruoff have recently derived a method for calculation of the van der Waals surface and volume of any fullerene.[6] The solubilities of fullerenes will be determined not only by these geometric factors but also by other factors involving the specific molecular interactions between the fullerene and the solvent molecules. The possible formation of solid solutions of the solvent with C_{60} may also play a key role. These questions can now be addressed for C_{60} and in the future will be addressable for larger fullerenes as they become available in substantial quantities.

To develop an understanding of these interactions for C_{60}, we report here measurements of the room temperature solubility of C_{60} in a range of solvents. The solubilities of C_{70} and higher fullerenes will be reported later.

Experimental Section

Pure C_{60} was obtained by using column chromatography with neutral alumina to purify "extract" obtained from primary arc-synthesized soot. It was dried at 350 K in a vacuum oven for 24 h, and its purity was determined by high-performance liquid chromatography (HPLC) and surface analysis by laser ionization (SALI) mass spectrometry to be 99.95%. Solvents used were generally of reagent grade (99% or better) and were used as received. Those of less than 99% purity are as follows: chloroform contained 1% ethanol stabilizer; nitromethane was 98.1% pure; pyridine was Baxter reagent grade; cyclopentane contained 98% pentanes, with at least 75% cyclopentane; 2-methylthiophene was 98% pure; 1,1,2-trichlorotrifluoroethane was industrial grade from Blaco-tron; 1-chloronaphthalene contained about 10% of the 2-chloro isomer; 1-phenylnaphthalene contained about 5% of the 2-phenyl isomer; tetralin was freshly distilled. The xylenes sample was a 22:63:15 mixture of the ortho, meta, and para isomers, and the decalins contained cis and trans isomers, in a 3:7 ratio.

A small quantity of C_{60} was added to each solvent to obtain an indication of how much would be required to ensure that extra solid would be present. If a strong color developed following a brief sonication, about 100 mg of C_{60} would be placed in a 1-dram bottle and 1–2 mL of solvent added. If only a faint color developed, only about 20 mg of C_{60} was used.[7] A $^3/_8$-in. Teflon-coated stirring bar was used to agitate the solutions in the dark for periods of not less than 24 h to ensure equilibration. The laboratory temperature varied between 293 and 298 K during this period. As a further test of attainment of equilibrium, the solubility of C_{60} in two commonly employed solvents, CS_2 and toluene, was measured after 24, 48, and 168 h. The solubility in each solvent at each of these time periods was found to be the same within experimental error. For several weak solvents, additional mixing was effected by sonicating the mixtures in an ultrasound cleaning bath for 5 min, followed by another 24-h stirring period. We did not observe any change in the measured solubilities as a result of the additional stirring, and hence the initial 24-h stirring was considered sufficient for equilibration. The saturated solution was filtered through a 0.45-μm poly(tetrafluoroethylene) (PTFE) filter (Gelman Acrodisc); a clean glass syringe was used to transfer the solution. The filtrate bottle was quickly closed with a Teflon-lined screw cap. Care was taken to ensure that solid residue was left in the bottle to serve as proof that the solution was not deficient in C_{60}(s) prior to filtering.

We initially intended to measure solubilities spectrophotometrically. However, we observed that the wavelength of the maximum of each C_{60} absorbance peak is significantly solvent-dependent. For example, the "328-nm" peak occurs at 328 nm in hexane, but at 335 nm in benzene. Also, many of the solvents strongly absorb in the 328-nm spectral region, such as those

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TABLE I: Solubility of C_{60} in Various Solvents

solvent	$[C_{60}]$, mg/mL	mole fraction ($\times 10^4$)	n	ϵ	V, cm^3 mol^{-1}	δ, cal$^{1/2}$ cm$^{-3/2}$
alkanes						
n-pentane	0.005	0.008	1.36	1.84	115	7.0
cyclopentane	0.002	0.003	1.41	1.97	93	8.6
n-hexane	0.043	0.073	1.38	1.89	131	7.3
cyclohexane	0.036	0.059	1.43	2.02	108	8.2
n-decane	0.071	0.19	1.41	1.99	195	8.0
decalins	4.6	9.8	1.48	2.20	154	8.8
cis-decalin	2.2	4.6	1.48	–	154	8.8
trans-decalin	1.3	2.9	1.47	–	158	8.6
haloalkanes						
dichloromethane	0.26	0.27	1.42	9.08	60	9.7
chloroform	0.16	0.22	1.45	4.81	86	9.3
carbon tetrachloride	0.32	0.40	1.46	2.24	80	8.6
1,2-dibromoethane	0.50	0.60	1.54	4.79	72	10.4
trichloroethylene	1.4	1.7	1.48	3.40	89	9.2
tetrachloroethylene	1.2	1.7	1.51	2.46	102	9.3
Freon TF (dichlorodifluoroethane)	0.020	0.042	1.36	–	188	–
1,1,2-trichlorotrifluoroethane	0.014	0.017	1.44	–	118	–
1,1,2,2-tetrachloroethane	5.3	7.7	1.49	8.20	64	9.7
polars						
methanol	0.000	0.000	1.33	33.62	41	14.5
ethanol	0.001	0.001	1.36	24.30	59	12.7
nitromethane	0.000	0.000	1.38	35.90	81	12.7
nitroethane	0.002	0.002	1.39	28.00	105	11.1
acetone	0.001	0.001	1.36	20.70	90	9.8
acetonitrile	0.000	0.000	1.34	37.50	52	11.8
N-methyl-2-pyrrolidone	0.89	1.2	1.47	–	96	11.3
benzenes						
benzene	1.7	2.1	1.50	2.28	89	9.2
toluene	2.8	4.0	1.50	2.44	106	8.9
xylenes	5.2	8.9	1.50	2.40	123	8.8
mesitylene	1.5	3.1	1.50	2.28	139	8.8
tetralin	16	31	1.54	2.76	136	9.0
o-cresol	0.014	0.029	1.54	11.50	103	10.7
benzonitrile	0.41	0.71	1.53	25.60	97	8.4
fluorobenzene	0.59	0.78	1.47	5.42	94	9.0
nitrobenzene	0.80	1.1	1.56	35.74	103	10.0
bromobenzene	3.3	4.8	1.56	5.40	105	9.5
anisole	5.6	8.4	1.52	4.33	109	9.5
chlorobenzene	7.0	9.9	1.52	5.71	102	9.2
1,2-dichlorobenzene	27[a]	53	1.55	9.93	113	10.0
1,2,4-trichlorobenzene	8.5	15	1.57	3.95	125	9.3
naphthalenes						
1-methylnaphthalene	33	68	1.62	2.92	142	9.9
dimethylnaphthalenes	36	78	1.61	2.90	156	9.9
1-phenylnaphthalene	50	131	1.67	2.50	155	10.0
1-chloronaphthalene	51	97	1.63	5.00	136	9.8
miscellaneous						
carbon disulfide	7.9	6.6	1.63	2.64	54	10.0
tetrahydrofuran	0.000	0.000	1.41	7.60	81	9.1
tetrahydrothiophene	0.030	0.036	1.50	2.28	88	9.5
2-methylthiophene	6.8	9.1	1.52	2.26	96	9.6
pyridine	0.89	0.99	1.51	12.30	80	10.7

[a] See ref 18.

containing nitro groups, CS_2, and several of the halogenated solvents. Consequently, we decided to use calibrated HPLC, a method free of such solvent effects.

The $[C_{60}]$ in the saturated filtered solution was analyzed by HPLC using a Waters System 6000 chromatograph equipped with a dinitroanilinopropyl (DNAP) column (9 mm × 250 mm; E. S. Industries), an ultraviolet (UV) detector set at 340 nm, and a Hewlett-Packard Model 3390 integrator. A solution of toluene (20% by volume) in hexane was used as the eluant. Detector response for $[C_{60}]$ was calibrated using several standard solutions in the range 0.01 to 0.20 mg/mL. If needed, the saturated solutions were diluted to bring the $[C_{60}]$ within the calibration range. Typically, several dilutions of each solvent were used, and measured solubilities were within 10% of each other. The average values computed are reported below.

Results

The measured solubilities are reported (in mg/mL and in mole fraction) in Table I, which is organized by solvent type. Several trends are apparent. C_{60} is essentially insoluble in polar and H-bonding solvents like acetone, tetrahydrofuran, acetonitrile, nitromethane, methanol, and ethanol. It is sparingly soluble in alkanes like pentane, hexane, and decane, with the solubility increasing with the number of carbons. The solubility in cyclopentane and in cyclohexane is also very low. In view of the rather poor solubility in alkanes and cycloalkanes, the solubility of 4.7 mg/mL in the 3:7 mixture of *cis*- and *trans*-decalins is truly remarkable. Replicate measurements were conducted to confirm the relatively high solubility. To test if the curved cavity of the cis decalin was particularly responsible for the high solubility, we determined the solubility of C_{60} in the *cis*- and *trans*-decalins separately. Interestingly, while the solubility of C_{60} is significantly higher in the cis isomer, it is still higher in the mixture than in either of the pure isomers.

The solubility in chloroalkanes (with the exception of the Freons) is generally higher than in alkanes, although it does not increase monotonically through the series CH_2Cl_2, $CHCl_3$, and CCl_4 (the values were 0.26, 0.16, and 0.32 mg/mL, respectively).

Among the C-2 chlorocarbons, the solubility in the ethylene derivatives is less than in the ethane derivative: solubility in trichloroethylene and tetrachloroethylene is a little over 1 mg/mL, but in 1,1,2,2-tetrachloroethane it is 5.3 mg/mL, the highest among this group of solvents.

C_{60} is appreciably soluble in aromatic solvents (with the notable exception of the H-bonding *o*-cresol). Substitution with electron-donating groups such as methyl and methoxy groups increases the solubility, while substitution with electron-withdrawing groups such as nitro and nitrile reduces it. Solubility increases in going from benzene to toluene and from toluene to xylenes, but introduction of the third methyl group (mesitylene) results in decreased solubility. Solubility of C_{60} in mesitylene is even less than in benzene. Substitution with chlorine and bromine increases solubility, while that with fluorine decreases it. Introduction of a second chlorine results in a substantial increase in solubility. Indeed, of the one-ring aromatic solvents tested here, *o*-dichlorobenzene has the highest solubility for C_{60}; the solubility approaches that achieved with naphthalene derivatives. However, as with the methyl substitutions, introduction of a third chlorine (1,2,4-trichlorobenzene) results in a sharp decrease in solubility.

The solubility in 2-methylthiophene, a heteroaromatic, is comparable to that in chlorobenzene. However, in pyridine, also a heteroaromatic, it is substantially less. In the nonaromatic heterocycles (tetrahydrothiophene and tetrahydrofuran), the solubility is markedly low. Among the nonaromatic solvents, the solubility is highest is carbon disulfide.

Increasing the size of the aromatic system (benzene to naphthalene) results in increased solubility. The relative effect of methyl and chloro substitution on naphthalene is similar to that on benzene. In accord with the general expectation, substitution with a phenyl has an effect similar to substitution with a chlorine. The "champion" solvent appears to be 1-chloronaphthalene, but when solubility is expressed as mole fraction, $[C_{60}]$ in 1-phenylnaphthalene is slightly higher.

Discussion

Solubility is influenced by several solvent properties. The H-bonding character of the solvent is an obvious discriminating factor. C_{60} will have a lower solubility in solvents that organize themselves through polar or H-bond interactions because of the disruption in the solvent structure that would result from dissolution of C_{60}, which is nonpolar and does not participate in H bonds. Many solvent parameters have been developed for a quantitative prediction of solubility of various solutes. Reichardt[8] has discussed several quantitative treatments of solvent parameters, and the reader is directed to this reference for a detailed discussion.

Solvent properties that might be expected to influence the solubility of C_{60} are polarizability, polarity, molecular size, and cohesive energy density. To investigate the influence of these properties, we chose the following solvent parameters: $(n^2-1)/(n^2+2)$, where n is the index of refraction (Na D line); $(\epsilon-1)/(\epsilon+2)$, where ϵ is the DC dielectric constant; δ, which is the Hildebrand solubility parameter (defined below); V, the molar volume, which is equal to the molecular weight divided by the density at 298 K. These parameters are a measure of the solvent polarizability, solvent polarity, cohesive energy density, and molecular size, respectively. As will be seen below, we have not found any one solvent parameter that universally explains the solubility of C_{60}. This result is not atypical of the interaction between a particular solute and a range of solvents.

The Hildebrand solubility parameter is defined as $\delta = (\Delta E/V)^{1/2}$, where ΔE is the cohesive energy and V the molar volume.[9] The cohesive energy is the energy required to convert a mole of liquid at 298 K to a mole of noninteracting gas. Normally, the enthalpy of vaporization, ΔH_{vap}, is the available

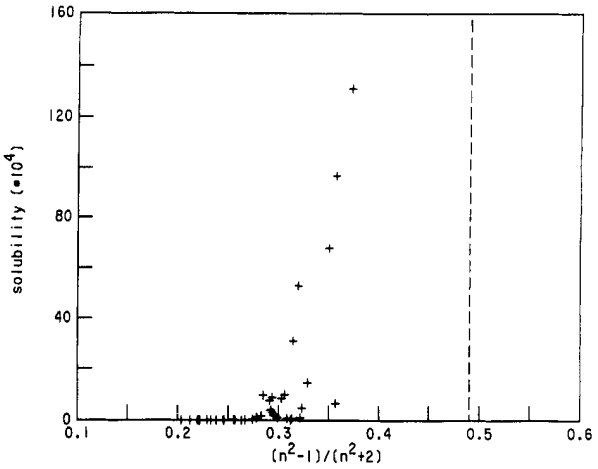

Figure 1. The 298 K solubility of C_{60} as a function of the solvent polarizability parameter. The polarizability parameter value for C_{60} is indicated by a dashed vertical line.

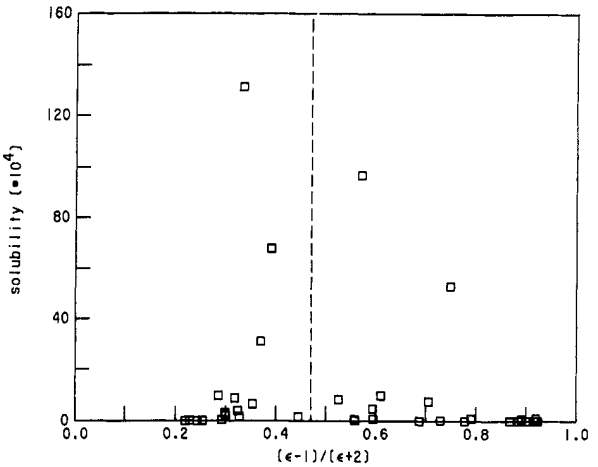

Figure 2. The 298 K solubility of C_{60} as a function of the solvent polarity parameter. The polarity parameter value for C_{60} is indicated by a dashed vertical line.

experimental quantity and δ is obtained as

$$\delta = \left[\frac{\rho(\Delta H_{vap} - RT)}{M}\right]^{1/2} \quad (1)$$

where ρ is the density at 298 K and M the molecular weight. Scott has derived an empirical method for correcting ΔH_{vap} values that are not 298 K values.[10] In calculating the δ values, we have taken recourse to this empirical correction factor when ΔH_{vap} (298 K) literature values were not readily available.

The values for n, ϵ, V, and δ are listed in Table I, along with the measured solubilities. Blank entries (–) result from our not finding literature values. In the figures presented below, the solubilities have been converted to mole fractions to remove the influence of density and molecular weight.

Figure 1 shows the variation of solubility with the polarizability parameter, $(n^2-1)/(n^2+2)$. Clearly, the higher the value of n, the higher the solubility. One notable outlier is carbon disulfide, which does not have as high a solubility (expressed as mole fraction) as might be expected from its high refractive index and a polarizability parameter of 0.36. For comparison purposes, the refractive index of C_{60} is 1.96, which gives a value of 0.49 for the polarizability parameter.

Figure 2 is a plot of the solubility as a function of the polarity parameter, $(\epsilon-1)/(\epsilon+2)$. Note that polarizability and polarity parameters are close to identical for solvents not possessing a permanent dipole moment. There is clearly more scatter in Figure 2 than in Figure 1, but in general the nonzero solubilities cluster in the polarity parameter range 0.3–0.8, i.e., that for solvents

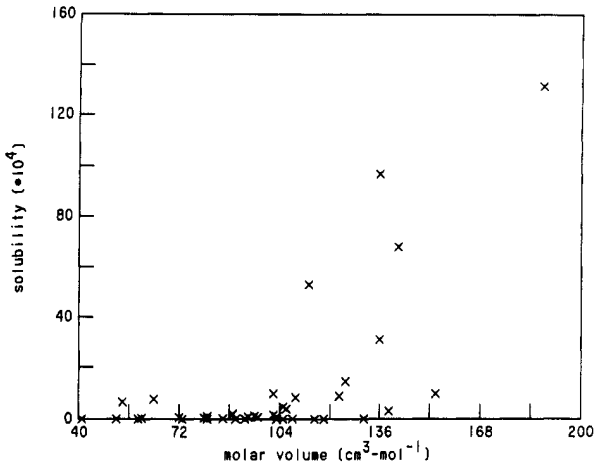

Figure 3. The 298 K solubility of C_{60} as a function of the molar volume of the solvent. The molar volume of solid C_{60} is 429 cm^3 mol^{-1} and is not explicitly shown in the figure..

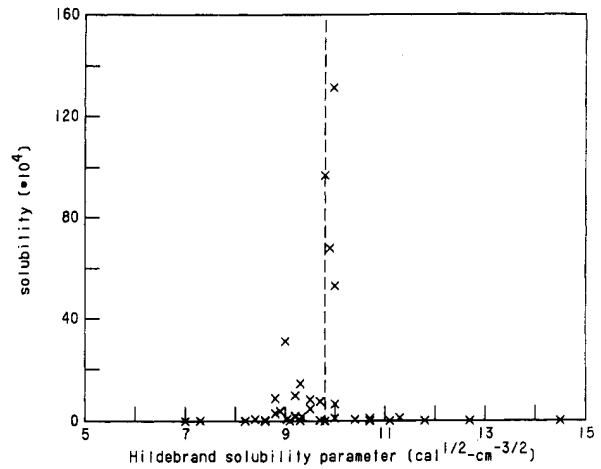

Figure 4. The 298 K solubility of C_{60} as a function of the Hildebrand solubility parameter. The square root of the cohesive energy density of C_{60} solid at 298 K is indicated by a dashed vertical line

with ϵ ranging from 2.5 to 10. Within this range, the solubilities do not display any systematic variation. For comparison purposes, for C_{60} with $\epsilon = 3.61$, $(\epsilon - 1)/(\epsilon + 2) = 0.47$.

Figure 3 shows the solubility as a function of V, the solvent molar volume. The data clearly indicate that an increase in solvent molecular size favors solvation of C_{60}. The molar volume of fcc C_{60}(s) is 429 cm^3 mol^{-1}, significantly higher than that of any solvent used here.

The solubility of C_{60} as a function of the Hildebrand solubility parameter, δ, is depicted in Figure 4. From Hildebrand's theory, one would expect the solubility to be greatest in a solvent whose δ value matches that of C_{60} and to decline progressively with increasing disparity in the δ values. Solvents with appreciable solubilities, such as toluene, phenylnaphthalene, chloronaphthalene, and CS_2, have δ values between 9.0 and 10.0, and from Figure 4 one might expect C_{60} to have a δ value of 10. However, some solvents, like acetone, nitrobenzene, and methylene chloride, have δ values close to 10.0 but very low solubility for C_{60}. On the other hand, decalin has a significantly different δ value, yet it has an appreciable solubility for C_{60}.

Comparison with an experimental value of δ for C_{60} is not as straightforward as comparisons for the other three solubility parameters. For use in solubility theory, the parameter δ is only defined for a liquid solute.[1] If the solute is a solid, a hypothetical supercooled liquid should be used as the reference liquid, and ΔH_{vap} for this hypothetical supercooled liquid should be used to determine δ. C_{60} has not yet been induced to melt, and therefore no experimental information exists from which to construct this hypothetical reference state. However, we find it intriguing that if ΔH_{vap} is replaced with ΔH_{sub} (the enthalpy of sublimation), a value of $\delta = 9.8$ $cal^{1/2}$ $cm^{-3/2}$ is obtained for C_{60}. For this calculation, we have used 41.4 kcal/mol for ΔH_{sub} and the reported density[11] of 1.68 g cm^{-3}. The average experimental value of ΔH_{sub} is 40 kcal/mol at a temperature of about 750 K,[12-14] and by using the Dulong–Petitt law of $3R = Cp$ as the intermolecular phonon contributions to the heat capacity in the temperature range from 298 to 750 K, we calculate the value at 298 K to be 41.4 kcal/mol.

The parameter δ is a measure of the energy required to create a cavity of given volume in a liquid, and when two liquids have identical values of δ, then the work to create equal sized volumes in each is isoenergetic. However, this solubility parameter does not directly address the chemical interactions between solvent and solute, but rather only the solute/solute and solvent/solvent interactions. It owes what predictive success it does have to judicious application for solutes and solvents that are "like". Figure 4 indicates that assigning a solubility parameter of 10 to C_{60} is not unreasonable, even given the scatter in the data. This value has interesting implications, which we briefly discuss below.

C_{60} is the most spherical molecule in existence and, as stated above, it has not yet been converted to a liquid. Unfortunately, few data are available on solubility or enthalpies for molecules that both form van der Waals solids and are "round", such as diamantane or dodecahedrane. Comparison with analogous systems is, therefore, not yet possible. We suggest that in cases where the energy of cohesion of the molecular solid (solute) is far greater than the energy of cohesion of the solvent, the appropriate method for calculating the Hildebrand solubility parameter is to use ΔH_{sub} directly. This hypothesis can be tested as the solubilities and requisite enthalpies of more systems are determined.

Another factor which might be playing a role in dissolution of C_{60} is the possible formation of a solid solution, where the solvent penetrates into the large interstitial sites of the solid phase which is in equilibrium with the solution. Formation of a solid solution lowers the thermodynamic driving force for dissolution. It is possible that solvent molecular size (and type) will play a critical role in formation of a solid solution, and the solubilities measured here might be indicating this, given the dependence of solubility on molecular size noted above. Further work is indicated on this issue.

While it is possible that multivariate statistical methods[15] such as multiple linear regression analysis or factor analysis might uncover "hidden" trends of the functional dependence of solubility of C_{60} on various solvent parameters, we are content to point out what is evident from Figures 1–4. All other things being equal, a solvent with a solvent parameter whose value is close to that of C_{60} will win over a solvent whose solvent parameter differs significantly. The data presented might aid in achieving the goal of rational choice of solvents for separation and purification of fullerenes.

The solubility of C_{60} in 15 organic solvents at 303 K has recently been determined by Sivaraman et al.[16] by UV–vis spectrophotometry of absorbance at 328 nm. Of the solvents common between the study presented here and ref 16, almost exact agreement is obtained for the alkanes (pentane, hexane, decane, cyclohexane), whereas for benzene, toluene, mesitylene, and CS_2 the values obtained here are on average 40% higher. We suggest two possible reasons for this discrepancy: First is a temperature dependence (see remarks below) of the solubility in these solvents.[17] Sivaraman et al. used a 303 K bath, which is 8 deg warmer than our average temperature. The second contributing factor could be the difference in equilibration times; we use a 24-h stirring period and Sivaraman et al. a 5-h stirring period.

Conclusion

The room temperature solubility of C_{60} in 47 different solvents has been determined by calibrated HPLC. For C_{60}, the index of refraction (Na d line frequency) is $n = 1.96$, the DC dielectric constant is $\epsilon = 3.61$, the molar volume is $V = 429$ cm^3 mol^{-1}, and the square root of the cohesive energy density *of the C_{60} solid* is $\delta = 9.8$ cal$^{1/2}$ cm$^{-3/2}$. The solubility data are plotted against solvent parameters that we have labeled the polarizability parameter ($[n^2-1]/[n^2+2]$), the polarity parameter ($[\epsilon-1]/[\epsilon+2]$), the molecular size parameter (v = molar volume), and the Hildebrand solubility parameter (δ = square root of cohesive energy density of solvent). These plots serve to emphasize that solvents whose n, ϵ, V, and δ approach those of C_{60} are relatively stronger solvents. However, the clear scatter in measured solubilities plotted against any single solvent parameter indicates that, although obvious trends are apparent, it is unlikely that a single "universal parameter" can be found for the wide range of solvents studied.

The substituted naphthalenes such as 1-methyl, 1-chloro, and 1-phenyl are solvents for which the room temperature solubility of C_{60} is about a factor of 7 higher than the solubility in CS_2 (expressed as mass C_{60}/volume solvent). When the solubility of C_{60} is expressed in mole fraction units, it is evident that C_{60} is not very soluble even in the strongest solvents studied here.

Further studies of larger fullerenes and extension of solubility studies to include variations in temperature and possibly pressure are suggested as prerequisites for the rational design of solvent-based systems for purification of fullerenes. For example, Ruoff et al.[17] have recently shown that the temperature dependence of the solubility of C_{60} displays a *maximum* in CS_2, toluene, and hexane at about 280 K, with the solubility first increasing to the maximum (endothermic dissolution) and then decreasing by about a factor of 2 from the maximum to the normal boiling point of the liquid. Another interesting possibility would be study of solubility at higher temperatures in polycyclic aromatic hydrocarbons which are solids at room temperature, such as naphthalene or chrysene.

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(18) We thank J. Tour for pointing out that our previous value for the solubility of C_{60} in 1,2-dichlorobenzene was incorrect. The value quoted in a preprint was remeasured to yield the value in Table I.