

## Solubility properties of C<sub>60</sub>\*

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The room temperature solubility of pure C<sub>60</sub> was determined in 47 solvents. The solubilities range from 0.01 mg/mL in methanol to 50 mg/mL in 1-chloronaphthalene. The solubilities in carbon disulfide, toluene, and hexane, three commonly employed solvents, are 7.9, 2.8, and 0.04 mg/mL, respectively. Solubilities of C<sub>60</sub> as a function of the solvent properties such as index of refraction, dielectric constant, Hildebrand solubility parameter, molecular size, and H-bonding strength show that "like dissolves like." No single solvent parameter can predict the solubility of C<sub>60</sub> with complete confidence but a composite picture of solvents with high solubility for C<sub>60</sub> emerges: large index of refraction, dielectric constant around 4, large molecular volume, Hildebrand solubility parameter equal to 10 cal<sup>1/2</sup>-cm<sup>3/2</sup>, and tendency to act as a moderate strength nucleophile. An unusual temperature dependence of C<sub>60</sub> in 3 common solvents is also discussed.

### 1. INTRODUCTION

The solubility of C<sub>60</sub> and other fullerenes is of practical, and fundamental, interest. Extraction and purification of solutes by solvents can constitute on the order of 50% of the overall cost of their production [1]. Extraction and chromatographic techniques currently employed for the isolation of C<sub>60</sub> [2-5] and of other pure fullerenes, are far too expensive for large scale production and utilization by the chemical industry. Thus, the interaction of fullerenes with various solvents will allow rational choice of solvents suitable for purifying the fullerenes by cheaper methods. Solubility data can also play a useful role in the choice of stationary phase and type of chromatography utilized. A more detailed account of our measurement of C<sub>60</sub> solubilities is given in [6].

### 2. RESULTS

Measured solubilities are reported (in mg/mL and in mole fraction) in Table 1. Several trends are apparent to the reader upon examination of Table 1; C<sub>60</sub> is essentially insoluble in polar and H-bonding solvents, and sparingly soluble in alkanes with the solubility increasing with the number of carbons. The solubility in cyclopentane and cyclohexane is also low. The solubility of 4.7 mg/mL in the 30:70 mixture of *cis* and *trans* decalins is, therefore, truly remarkable. To test if the curved cavity of the *cis* decalin was particularly responsible for the high solubility, we determined the solubility of C<sub>60</sub> in the *cis* and *trans* decalins separately. Interestingly, while the solubility of C<sub>60</sub> is significantly higher in the *cis* isomer, it is still higher in the mixture than in either of the pure isomers.

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Table 1.<sup>a</sup>  
Solubility of C<sub>60</sub> in various solvents

Solvent	[C <sub>60</sub> ] mg/mL	Mole fraction (×10 <sup>4</sup> )	Solvent	[C <sub>60</sub> ] mg/mL	Mole fraction (×10 <sup>4</sup> )
<b>alkanes</b>			N-methyl-2-pyrroli-		
n-pentane	0.005	0.008	done	0.89	1.2
cyclopentane	0.002	0.003	<b>benzenes</b>		
n-hexane	0.043	0.073	benzene	1.7	2.1
cyclohexane	0.036	0.059	toluene	2.8	4.0
n-decane	0.071	0.19	xylenes	5.2	8.9
decalins	4.6	9.8	mesitylene	1.5	3.1
cis-decalin	2.2	4.6	tetralin	16	31
trans-decalin	1.3	2.9	o-cresol	0.014	0.029
<b>haloalkanes</b>			benzonitrile	0.41	0.71
dichloromethane	0.26	0.27	fluorobenzene	0.59	0.78
chloroform	0.16	0.22	nitrobenzene	0.80	1.1
carbon tetrachloride	0.32	0.40	bromobenzene	3.3	4.8
1,2-dibromoethane	0.50	0.60	anisole	5.6	8.4
trichloroethylene	1.4	1.7	chlorobenzene	7.0	9.9
tetrachloroethylene	1.2	1.7	1,2-dichlorobenzene	27	53
Freon TF (dichloro-			1,2,4-trichloroben-		
difluoroethane	0.020	0.042	zene	8.5	15
1,1,2-trichlorotri-			<b>naphthalenes</b>		
fluoroethane	0.014	0.017	1-methylnaphthalene	33	68
1,1,2,2-tetrachloro-			dimethylnaphthalene	36	78
ethane	5.3	7.7	1-phenylnaphthalene	50	131
<b>polars</b>			1-chloronaphthalene	51	97
methanol	0.000	0.000	<b>miscellaneous</b>		
ethanol	0.001	0.001	carbon disulfide	7.9	6.6
nitromethane	0.000	0.000	tetrahydrofuran	0.000	0.000
nitroethane	0.002	0.002	tetrahydrothiophene	0.030	0.036
acetone	0.001	0.001	2-methylthiophene	6.8	9.1
acetonitrile	0.000	0.000	pyridine	0.89	0.99

<sup>a</sup>adapted from Ref. 6.

The solubility in chloroalkanes (with the exception of the freons) is generally higher than in alkanes.

C<sub>60</sub> is appreciably soluble in aromatic solvents (with the notable exception of the H-bonding *o*-cresol). 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. In fact, solubility of C<sub>60</sub> in mesitylene is even less than in benzene. Substitution with chlorine and bromine

increases solubility, but fluorine decreases it. A second chlorine results in a substantial increase in solubility. Of the one-ring aromatic solvents tested here, *o*-dichlorobenzene has the highest solubility for C<sub>60</sub> with the solubility approaching 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.

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, interestingly, 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 strongest solvent appears to be 1-chloronaphthalene, but with solubility expressed as a mole fraction,  $[C_{60}]$  in 1-phenylnaphthalene is actually slightly higher.

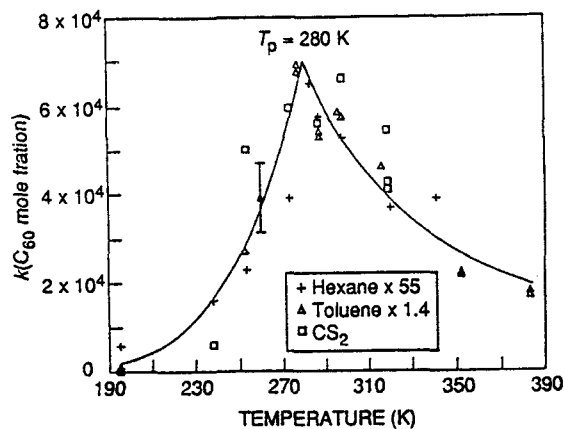
Many solvent parameters have been developed for a quantitative prediction of solubility of various solutes. Solvent properties that might be expected to influence the solubility of  $C_{60}$  are polarizability, polarity, cohesive energy density, and molecular size. The influence of these properties has been discussed extensively in [6].

A factor which could be playing a role in dissolution of  $C_{60}$  is possible formation of a solid solution, where solvent molecules penetrate into the large interstitial sites of the solid phase in equilibrium with the solution. Formation of a solid solution will likely lower the thermodynamic driving force for dissolution. For example, formation of a solid solution is indicated from variable temperature studies of the solubility of  $C_{60}$  in toluene, hexane, and  $CS_2$ , respectively.

For organic solutes in organic solvents the common experience is that solubility increases on warming; dissolution is normally endothermic. We have investigated the temperature-dependent solubility of  $C_{60}$  and observed an unusual solubility maximum near room temperature for hexane, toluene, and  $CS_2$ , respectively [7]. Although solubilities of  $C_{60}$  in these three solvents differ by several orders of magnitude, the relative solubilities are about the same, leaving us to conclude that dissolution is endothermic below room temperature and exothermic above. A solubility maximum (or minimum) for organic compounds in non-electrolytes is unprecedented; a more detailed description is given in [7].

The temperature dependence of the solubilities (mole fractions) is shown in

Figure 1. In all three solvents, the solubility of  $C_{60}$  is minimal at  $-78^\circ C$ . Warming the solution increases the solubility in all three solvents, but to different extents. The trend continues till roughly  $10^\circ C$ , above which it is roughly flat till  $25^\circ C$  and then clearly decreases by roughly a factor of 2 to 3 from  $25^\circ C$  to the normal boiling point of toluene and hexane.



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Figure 1. Temperature dependent solubility of  $C_{60}$  in hexane.

The likely cause of the unusual temperature dependence of the solubility are the changes in the solid phase. We suggest this hypothesis as a result of recognizing the nearly conformal temperature dependence of  $k$  in three different solvents although the absolute values of  $k$  in these solvents vary by about two orders of magnitude.

## REFERENCES

- [1] J.M. Prausnitz, R.N. Lichtenthaler, and E. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria* (Prentice Hall, Englewood Cliffs, NJ, 1986).
- [2] R. Taylor, J.P. Hare, A.K. Abdul-Sada, and H.W. Kroto, *J. Chem. Soc., Chem. Commun.* 1990, 1423.
- [3] W.H. Pirkle, and C.J. Welch, *J. Org. Chem.* 1991, 56, 6973.
- [4] A. Koch, K.C. Khemani, and F. Wudl, *J. Org. Chem.* 1991, 56, 4543.

- [5] P. Bhyrappa, A. Penicaud, M. Kawamoto, and C.A. Reed, *J. Chem. Soc. Chemical Communications*, submitted.
- [6] R.S. Ruoff, D.S. Tse, R. Malhotra, and D. C. Lorents, *J. Phys. Chem.* **97**, 3379 (1993)
- [7] R.S. Ruoff, R. Malhotra, D.L. Huestis, D. S. Tse, and D. C. Lorents, *Nature* **362**, 140 (1993).