

Solubility and molecular state of C₆₀ and C₇₀ in solvents and solvent mixtures

Mihály T. Beck

Department of Chemistry, Kossuth Lajos University, Debrecen, 4010 Hungary

Abstract: The solubility of C₆₀ and C₇₀ has been studied very thoroughly. Beside the obvious practical importance, there is a great theoretical interest in the determination and explanation of the solubility data. The anomalous dependence of solubility on temperature is due to the formation of solid solvates and interaction between the fullerenes and solvents leading to the formation of a series of well defined complexes. One always should consider the possibility of colloid formation, particularly when sonication is applied to enhance the rate of dissolution. Sonication offers a possibility to achieve higher concentration of dissolved fullerenes. However, prolonged sonication may result in a decrease of concentration.

INTRODUCTION

It is likely that C₆₀ is one of the molecules the solubility of which has been determined in the highest number of solvents. Data for C₇₀ are more scarce but equally interesting. The reason of the interest in this problem has several obvious practical and theoretical motives. The interpretation of the experimental findings requires experiments using the whole armoury of chemical research. The analysis of the data reveals a number of general problems of modern research and publication. In this paper the present state of knowledge in this field is summarized and an effort is made to explain the contradictory results. Most of the solubility data for C₆₀ were recently reviewed (ref. 1). At present data are available for the solubility of C₆₀ in about 150 solvents and solvent mixtures while for C₇₀ in about 30 systems.

EXPERIMENTAL PITFALLS

As it appears from the data of Table 1, solubilities determined by different authors may exhibit fairly big differences. The most likely reason of the deviations is that different methods were applied to enhance the rate of dissolution of C₆₀. Namely, the dissolution of fullerenes is rather slow and the rate depends on the history of the sample pretreatment: heating and grinding. To decrease the time necessary to achieve the equilibrium intensive shaking, stirring or sometimes sonication are applied. However, sonication certainly may result in formation of colloid solutions leading to higher value for the solubility. Interestingly, using tetrahydrothiophene as solvent, sonication leads to a smaller value of the solubility. We have thoroughly studied the effect of sonication on the solubility of C₆₀ in a mixture of *cis*- and *trans*-decaline. Sonication for about 100 min greatly increases the solubility (ref. 2). We found, however, that prolonged sonication results in a decrease of the solubility. Similar behaviour have been found by us in several other solvents (ref. 3). It is likely that in these cases sonication initiated chemical reactions which may result in the change

*Lecture presented at the 8th International Symposium on Solubility Phenomena, Niigata, Japan, 5–8 August 1998. Other presentations are published in this issue, pp. 1867–1932.

of the composition of the solute and/or the solid phase. Mandrus et al. found a change of the color of the solution when decaline was sonicated for several hours and the formation of $C_{60}H_2$ was detected (ref. 4). It is practically certain that the solubility maximum found in a certain mixture of the *cis*- and *trans*-decaline (ref. 2) is an artifact.

TABLE 1
Solubility of C_{60} determined by different authors

Solvent	Solubility (mg/ml)
benzene	1.50*
benzene	0.88
toluene	2.90*
toluene	0.54
1,2-chlorobenzene	24.60*
1,2chlorobenzene	7.11
1,2,4-trichlorobenzene	10.40*
1,2,4-trichlorobenzene	4.85
tetrahydrothiophene	0.03*
tetrahydrothiophene	0.11

* indicate that sonication was applied. Data are from ref. 1.

Fullerenes are fairly reactive molecules. As it will be discussed in the next part of this paper, there are solvents in which either molecular complexes or new covalent adducts are formed. The reactivity of the solvent may depend on the experimental conditions. The possible effects of temperature, illumination or sonication always should be clarified to get meaningful solubility values.

MOLECULAR STATE OF C_{60} AND C_{70} IN SOLUTION

There are two problems concerning the molecular states of fullerenes in solution. One should determine the degree of self-association, and determine the nature and extent of interaction between the fullerene and the solvent molecules. Both types of interaction depend on the nature of solvent molecules. In the case of the *inert* solvents only weak van der Waals forces between the solvent and the fullerene molecules should be considered, and the spectra of these solutions correspond to the spectra of fullerenes in the gas phase. In the case of another group of solvents, although there is a change in the spectra, no well defined solvated species are formed, while in the third group of the solvents, which may be termed as *reactive solvents*, usually a series of chemically well characterized species, consisting of the fullerenes and molecules of the solvent are formed. It is expected that there is a less probability of the association of fullerenes themselves in the case of reactive solvents. First the problem of the aggregation is examined.

Self-association of fullerenes in solution. There are a number of possibilities to get information on the association of molecules in solution. Unfortunately, the different types of measurements led to rather contradictory results. Honeychuck et al. (ref. 5) determined the molecular weight of C_{60} in benzene and chlorobenzene solution by vapor pressure osmometry. In benzene 710 ± 10 , while in chlorobenzene 930 ± 5 was obtained. It is just a coincidence that the sum of the molecular weights of C_{60} and two molecules of chlorobenzene is quite close to 930, since such a species cannot be detected by vapor pressure osmometry. It follows from these findings that in benzene C_{60} is present in monomeric form, while in chlorobenzene the higher value may indicate a partial dimerization. However, Catalán et al. (ref.67) found that the Beer-Lambert law is strictly valid in all the studied solvents, including chlorobenzene, in a very

broad concentration range (2.63×10^{-5} - 5.08×10^{-3} mol.l⁻¹) in the whole visible region. This is a strong evidence that no change in the molecular state of the solute occurs. Sedimentation experiments exclude the formation of higher aggregates (ref. 7). Diffusion rate of both C₆₀ and C₇₀ evaluated from ¹³C NMR spin-echo measurements (ref. 8,9) indicate that in benzene solution both fullerenes exist in monomeric form. On the other hand, light-scattering experiments led to quite different results. Ying et al. found (ref. 10) that in benzene solution there is a slow aggregation of C₆₀ leading to the formation of particles the diameter of which is about 180 nm. Shaking of solutions, however, resulted in disaggregation. From our light-scattering experiments the formation of even bigger aggregates can be calculated. It seems most likely, however, that these values are artifacts and are caused by the very peculiar fluorescence and non-linear optical properties of the fullerene solutions.

Formation of aggregates of C₇₀ in toluene and in toluene - acetonitrile solvent mixtures. Sun and Bunker (ref. 11) arrived at this conclusion based on the solvatochromic effect occurring abruptly at certain concentration of acetonitrile. Light-scattering experiments by Ghosh et al. (ref. 12) were interpreted by the formation of aggregates the particle size of which varies between 100 and 1000 nm. In toluene and in solvent mixtures up to 50 % acetonitrile particles of < 6 nm were found, but the increase of the concentration of acetonitrile first led to a bimodal behaviour and over 70 % to the formation of higher aggregates, only. Unfortunately, all these measurements, were made at only one concentration of C₇₀ (3.5×10^{-6} M⁻¹). Obviously the dependence on the behaviour as a function of fullerene concentration would be vitally important to make sound conclusions on the formation of aggregates. The fact that the solubility of C₆₀ and C₇₀ in solvent mixtures rich in polar constituent is rather small, makes a difficulty for such experiments. Mándi and Beck (ref. 13) determined the validity of Beer-Lambert law in different solvent mixtures of toluene and different nitriles. It was found that the law is strictly valid in toluene - benzonitrile mixtures even up to the highest possible concentration of C₆₀ (4×10^{-4} M⁻¹), but in the case of toluene - acetonitrile mixtures a deviation was found at higher concentration of acetonitrile over 1.4×10^{-5} M concentration of C₆₀. This finding may indicate the formation of aggregates, but sedimentation or diffusion rate experiments could give more definite evidence either pro or con.

Association between fullerenes and other molecules in solution. There are possibilities for the formation of molecular complexes involving fullerenes and solvent molecules when e.g. different amines are used as solvents. The stability constants of these species can be determined by using solvent mixtures. One solvent should be inert, and the other solvent is the amine in question. The studies (e.g. ref. 14, 15) indicate the formation of rather weak complexes. It is likely, nevertheless, that in the pristine amines the formation of more than one complex should be considered. There appears no correlation between the solubilities and the values of the stability constants. The formation of a weak complex of C₆₀ with iodine was detected (ref.16). However, it is so unstable that the stability constant could not be determined. Surprisingly the formation of a rather stable complex of the composition C₆₀(I₂)₃ was reported and its stability constant evaluated from extraction and solubility experiments (ref. 17). These results, however, are definitely erroneous (ref. 18).

C₆₀ and C₇₀ are soluble in cyclopolienes. The reaction of cyclopentadiene with fullerenes were studied earlier and well defined Diels-Alder adducts were prepared (ref. 19). No data for the stability constants of these adducts are available. Such information could be obtained from experiments applying mixed solvents, consisting of an inert solvent and the cyclopolienes in question.

Both the molecular complexes and the Diels-Alder adducts are strictly analogous to the metal complexes and the same experimental and calculation methods can be applied for the evaluation of the corresponding stability constants. The role of the metal center is played by the fullerene molecule. The coordination chemistry of fullerenes is a most promising field.

SOLID SOLVATE ADDUCTS OF FULLERENES

There are plenty of evidence for the formation of solid adducts of C_{60} with a number of different solvents. Even molecules of inert solvents may form clathrates with fullerenes by occupying void spaces among the fullerene molecules in the crystal lattice. Quantitative data are available for C_{60} but the situation is obviously similar for C_{70} and other fullerenes. Well defined solids can be obtained either by slowly evaporating the given solvent, or by using the solution of fullerenes in another solvent in which the fullerene is more soluble and adding the given solvent as a precipitant. Data for the composition of different solvates are summarized in Table 2. The temperature of the procedure is critical since the composition of the solids strongly depends on the temperature. Usually more than one kind of solvates are in the solid phase and when two solvents are used mixed solvates can be formed.

TABLE 2.

Solid solvates of C_{60} : $C_{60}X_n$

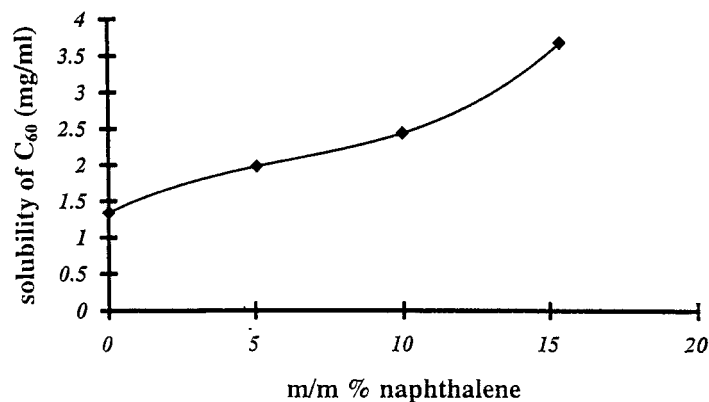
X	n	Solvent (precipitant)	ref.
benzene	4	X	20
carbon disulfide	1.09	X (isooctane)	21
n-pentane	0.98	toluene (petroleum ether)	22
1,3-dibromopropane	0.75	toluene (isooctane)	22
diethylether	0.48	toluene (X)	22
acetone	0.69	toluene (X)	22
2-butanone	1.09	toluene (X)	22
cyclohexane	2 and 13.7	X	23
carbon tetrachloride	13	X	24
n-octane	1	X	25
o-xylene	2	X	26
1,2-dichlorobenzene	2	X	27

DEPENDENCE OF SOLUBILITY ON TEMPERATURE

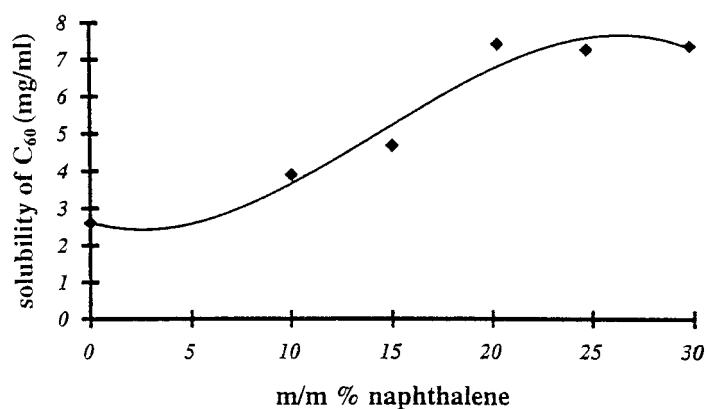
It was a most interesting finding by Ruoff et al. that the solubility of C_{60} exhibits a maximum (ref. 28). It was a coincidence that the solubility in hexane, toluene and carbon disulfide exhibits a maximum at around 280 K, although the absolute values are rather different. A phase transition of C_{60} takes place at 260 K. Ruoff et al. assumed that the wetting by the solvent may change the transition temperature and heat. Korobov et al. (ref. 29) explained the anomalous effect of solubility on temperature by the formation of different solid adducts. There is no doubt that this is a basically sound explanation, however, the situation is more complicated. Depending on temperature there is a possibility of the formation of a number of solvates and even the solvation of the dissolved fullerenes may depend on the temperature. The solubility maximum has been found with a number of solvents and there are wide differences among the values. Doome et al (ref. 30) found that in 1,3-diphenylacetone it is as high as 409 K. It is likely that the anomalous temperature dependence does occur if the temperature range is wide enough.

In principle there is a possibility of the appearance of more than one limiting value on the solubility vs. temperature plots. In fact, such a behaviour is found among the published data, however, the differences in the solubility values at different temperatures are rather small and may be due to experimental errors.

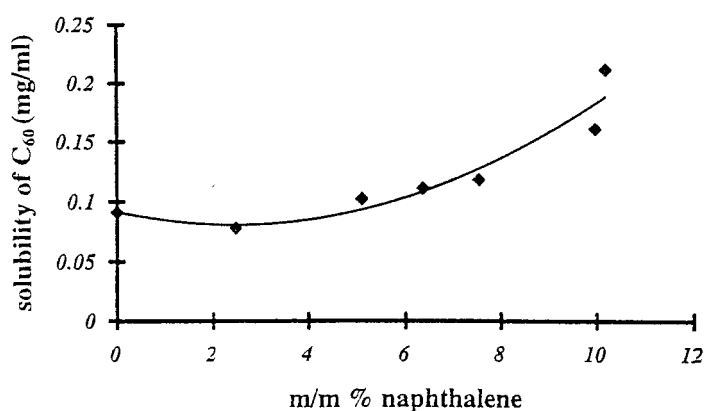
a)



b)



c)



Dependence of solubility of C₆₀ on the concentration of naphthalene in
a) decaline ; b) toluene ; c) dodecane solvent mixtures

For C_{70} the first studies did not reveal an anomalous temperature dependence. However, Doome et al. (ref. 30) found a maximum in solubility in each of the three solvents (tetralin, o-dichlorobenzene, 1,3-diphenyl-acetone) studied. It seems likely that such solubility behaviour occurs with all fullerenes, since in all cases there are plenty of possibilities for formation of solid and dissolved adducts, the composition of which depends on temperature.

A different explanation of the temperature maximum was offered by Bezmelnitsyn et al. (ref. 31). According to this explanation C_{60} clusters are formed in the solution. The size of these aggregates depends on temperature and this causes the change of solubility as a function of temperature. They could achieve very good fit between the measured and calculated curves, but they did not use independent experimental data for cluster formation. Furthermore there is convincing evidence that in the cases studied C_{60} is present in a monomeric form, so this explanation is not convincing.

SOLUBILITY IN SOLVENT MIXTURES

As it was mentioned above, the report that the solubility of C_{60} exhibits a maximum in a 3:7 mixture of *cis*- and *trans*-decaline is not substantiated. In fact the solubility in these mixtures is almost strictly additive and is approximately the sum of the solubilities in the two isomers. However, in all the other solvent mixtures studied, solubilities are more complex functions of solvent composition.

In mixtures of different nitriles and toluene the solubilities of C_{60} and C_{70} exponentially increase with increase in the concentration of toluene. There is certainly an interaction between the fullerenes and the nitriles: the spectral changes run parallel with the change of solubility. It would be interesting to prepare solid solvates. Experiments for this end are in progress in our laboratory.

As it is shown on Fig. 1, when naphthalene is dissolved in decaline, toluene or dodecane, the solubility of C_{60} characteristically changes as a function of the concentration of naphthalene (ref. 32). There are inflexion points, and in two cases at least one limiting value on the curves. There is a weak interaction between naphthalene and C_{60} in the solution indicated by the spectral effect. In addition the composition of the solid phase is certainly a function of the naphthalene concentration. The study of these solvates is also in progress.

SOLUBILITY CORRELATIONS

There are some obvious correlations between the the solubility of the fullerenes and the chemical characteristics of the solvents (ref. 2). In polar solvents particularly those having H-bonding character, the solubility is very small. In saturated hydrocarbons the solubility in general is smaller than in aromatic solvents. Naphthalene derivatives appear to be the best solvents for the fullerenes. The order of solubility in solvents containing a halogen which have similar composition is usually, but not always, $I > Br > Cl$.

Marcus carefully analyzed the data for all organic solvents (ref. 33) and established a rather good linear relation between the logarithm of the solubility and the weighted sum of four solvent parameter (molar refractio, polarity/polarizabilty, polarity and dipole moment). This relationship is valid for 55 solvents. Errors in the values of the solubilities may be responsible for some of the outlying data points. It is evident that to establish well founded correlations between different properties of solvents and solubilities it is a prerequisite to make use of reliable solubilities having exact thermodynamic significance. Therefore a critical evaluation of published stability constants with a determination of their thermodynamic significance is badly needed.

Acknowledgement

I would like to express my gratitude to my collaborators , Dr. S Kéki, G. Mándi and P. Kovács for their enthusiastic help and to the Hungarian National Research Foundation for the grants No. T7516 and T25222.

REFERENCES

1. M. T. Beck and G. Mándi. *Fullerene Science and Technology*, **5**, 291 - 310 (1997).
2. R.S. Ruoff, R. Malhotra, D. S. Tse and D. C. Lorents. *J. Phys. Chem.* **97**, 3379 - 3383 (1993).
3. G. Mándi and M.T. Beck. to be published.
4. D. Mandrus, M. Kele, R.L.Hettlich, G. Guichon, B.C. Sales and L.A. Boatner. *J. Phys. Chem. B* **101**, 123-128 (1997).
5. R. V. Honeychuck, Th. W. Cruger and JoAnn Milliken. *J. Am. Chem. Soc.* **115**, 3034 3035 (1993).
6. J. Catalán, J. L. Saiz, J. L. Laynez, N. Jagerovic and J. Elguero. *Angew. Chem. Int. Ed.* **34**, 105 - 106 (1995).
7. J. Kardos, P. Závodszky and M. T. Beck. to be published.
8. T. Kato, K. Kikuchi and Y. Achiba. *J. Phys. Chem.* **97**, 878 - 881 (1994).
9. R. Haselheimer, M. Holz, M. M. Kappes and R. H. Michel. *Ber. Bunsenges. Phys. Chem.* **98**, 878 - 881 (1994).
10. Q. Ying, J. Marecek and B. Chu. *Chem. Phys. Lett.* **219**, 214 - 218 (1994).
11. Y.-P. Sun and C. E. Bunker. *Nature* **365**, 398 - 399 (1993).
12. H.N. Ghosh, A.V. Sapre and J.P. Mittal. *J. Phys. Chem.* 9437 - 9440 (1996).
13. G. Mándi and M.T. Beck. In *Fullerenes* Vol. 5. (K.M. Kadish and R.S. Ruoff, eds.) pp. 382 - 388. The Electrochemical Society, Pennington, N.J. (1997).
14. Y.-P. Sun, C.E. Bunker and B. Ma. *J. Am. Chem. Soc.* **116**, 9692 - 9699 (1994).
15. G. Mándi and M.T. Beck. In *Fullerenes* Vol 5. (K.M. Kadish and R.S. Ruoff, eds) pp. 380 - 396. The Electrochemical Society, Pennington, N.J. (1997).
16. M. T. Beck, S. Kéki and É. Balázs. *Fullerene Science and Technology*, **1**, 119 - 124 (1993).
17. A.N. Turanov and J.N. Kremenskaya. *Russ. Chem. Bull.* **44**, 465 - 466 (1995).
18. M.T. Beck, G. Mándi and S. Kéki. *Russ. Chem. Bull.* **45**, 2024 - 2025 (1996).
19. M. F. Meidine, R. Roers, G. J. Langlely, A. G. Avent, A R. Darwish, S. Firth, H. W. Kroto, R. Taylor and D. R. M. Walton. *J. Chem. Soc. Commun.* 1342 -1343 (1993).
20. M. Meidine, P.B. Hitchcock, H.W. Kroto, R. Taylor and D.R.M. Walton. *J. Chem. Soc. Chem. Commun.* 1564 - 1565 (1992).
21. B. Morosin, P. P. Newcomer, B. J. Baughman, E. L. Venturini, D. Loy and J. E. Schriber. *Physica C*. **184**, 21 (1995).
22. S. Pekker, G. Faigel, G. Oszlányi, T. Kemény and E. Jakab. *Synthetic Metals* **55-57**, 3014 - 3020 (1993).
23. Y. Nagano, T. Tamuta and T. Kiyobayashi. *Chem. Phys. Lett.* **228**, 125-130 (1994).
24. Y. Nagano and T. Tamura. *Chem. Phys. Lett.* **252**, 362 - 366 (1996).
25. R. Céolin, V. Agafonov, S. Toscani, M. - F. Gardette, A. Gonthier-Vassal and H. Szwarc. *Fullerene Science and Technology*. **5**, 559 - 565 (1997).
26. M. V. Korobov, A.L. Mirakian, N.V. Avramenko, I.S. Neretin, E.B. Stukalin and R.S. Ruoff. In. *Fullerenes* Vol. 4. (K. M. Kadish and R. S. Ruoff, eds) pp. 40 - 550. The Electrochemical Society, Pennington, N.J. (1997).
27. A. L. Smith, K. Strawhecker, H. Shirazi, G. Olofsson, I. Wadsö and E. Quarnström. In *Fullerenes* Vol. 4. (K. M. Kadish and R.S. Ruoff, eds) pp. 599 - 606. The Electrochemical Society, Pennington, N.J. 1997.
28. R. S Ruoff, R. Malhotra, D. L. Huestis, D. S. Tse and D. C. Lorents. *Nature* **362**, 140 -141 (1993).
29. M. V. Korobov and O. L. Gurvich. In *Fullerenes* Vol. 3. (K. M. Kadish and R. S. Ruoff, eds) pp. 1544 - 1550. The Electrochemical Society, Pennington, N.J. (1995).
30. R. J. Doome, S. Dermaut, A. Fonseca, M. Hammida and J. B. Nagy. *Fullerene Science and Technology* **7**, 1593 - 1606 (1997).
31. V. N. Bezmelnitsyn, A. V. Eletsii and E.V. Stepanov. *J. Phys. Chem.* **98**, 6665 - 6667 (1994).
32. M. T. Beck and P. Kovács. to be published.
33. Y. Marcus. *J. Phys. Chem.* **101**, 8617 - 8623 (1997).