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Aqueous solubilization of [60]fullerene *via* inclusion complex formation and the hydration of C_{60}

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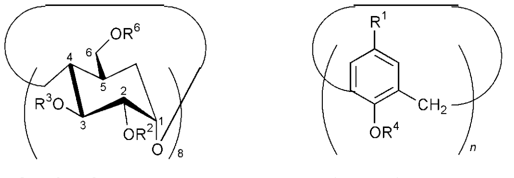
Natural and substituted cyclodextrins (CDs), as well as some calixarenes, have been investigated with respect to their solubilization of C_{60} in water. Underivatized γ-CD is proved to have unique solubilizing power among the possible complexing agents as it produces stable solutions and solids containing real 1 : 2 complexes. The differences in the appearance of the solutions (magenta or brown colour) are explained by the hydration of the C_{60} within the supramolecule. The composition and structure of the complexes are proved by chemical analyses, X-ray diffraction, atomic force microscopy and solid state NMR.

Introduction

Since 1991, several papers have been published on the solubilization of highly hydrophobic C_{60} in water by means of different complexing agents. Primarily γ-cyclodextrin (cyclomaltooctaose, γ-CD, **I** in Scheme 1) has been investigated[1] (considering its hydrophobic inner cavity and its size), but experiments with methylated β-CDs,[2a,b] with cyclodextran (cycloisomaltooctaose[2c]) and also with δ-CD (cyclomaltononaose, complexing C_{70}, too)[2d] have been reported. [The results with γ-CD published up to 1997 have been given in detail[3a] and other aspects of supramolecular fullerene chemistry (including complex formation with calixarenes) have also been discussed in a recent review.[3b]] In spite of the fact that complex formation between C_{60} and different calixarenes has been extensively studied,[3b,4b,c] only one water-soluble species [namely the complex with octakis(3-sulfonatopropyloxy)-calix[8]arene, **IV** in Scheme 1] is mentioned.[1m,4a]



I: $R^2 = R^3 = R^6 = –H$
γ-cyclodextrin
II: $R^2 = CH_3\text{-}CH(OH)\text{-}CH_2\text{-}$ or H-
$R^3 = CH_3\text{-}CH(OH)\text{-}CH_2\text{-}$ or H-
$R^6 = CH_3\text{-}CH(OH)\text{-}CH_2\text{-}$ or H-
hydroxypropyl-γ-cyclodextrin
III: $R^2 = R^3 = R^6 = CH_3\text{-}$
trimethyl-γ-cyclodextrin
IV: $n = 8$; $R^1 = \text{-H}$; $R^4 = \text{-}(CH_2)_3SO_3Na$
octakis(3-sulfonatopropyloxy)calix[8]arene
V: $n = 8$; $R^1 = \text{-}SO_3H$; $R^4 = \text{-H}$
octahydroxyoctasulfocalix[8]arene
VI: $n = 6$; $R^1 = \text{-}SO_3Na$; $R^4 = \text{-}C_{12}H_{25}$
hexasulfonatohexakis(dodecyloxy)calix[6]arene

Scheme 1 Host molecules used to solubilize C_{60} in water.

Several methods have been described for the preparation of water-soluble C_{60} complexes, including refluxing,[1a,c,e,4] stepwise changing of solvents or liquid–liquid extraction,[1b,f,j,k] kneading[1d] or mechanochemical treatment by ball or high-speed vibration milling.[1g,l,m] There is still some uncertainty in the literature[1a,c] as to whether these solutions contain real complexes or aggregates. Moreover, preparation of stable colloidal aqueous solutions of C_{60} without any stabilizing agent (merely by careful, gradual changing of the solvents) has also been described.[5]

In parallel with preparation experiments have been detailed studies of the reaction products.[1–6] Only two important results are mentioned here: (i) that the interaction between C_{60} and γ-CD could be proved by NMR[1h] and (ii) that the $C_{60}\cdot(\gamma\text{-CD})_2$ species has also been detected by MS in the gas phase.[6b]

We have carried out experiments with C_{60} and γ-CD and reported our initial results.[1e,g,l] The first aim of this work was to find the background of the reversible (or irreversible) changes of the complexed [60]fullerene (both in solution and in the solid state). We also summarize here the results of experiments conducted over a longer period, results obtained with some other complexing agents [hydroxypropyl- and trimethyl-γ-CD and some calixarenes, (see Scheme 1)], and some new ideas for the interpretation of our results.

Experimental

Cyclodextrins (Cyclolab Ltd., Budapest, Hungary) and pure polycrystalline C_{60} (F&J Ltd, Moscow, Russia) were used as received. 5,11,17,23,29,35-Hexasulfonato-37,38,39,40,41,42-hexahydroxycalix[6]arene, 5,11,17,23,29,35-hexasulfonato-37,38,39,40,41,42-hexakis(dodecyloxy)calix[6]arene and 5,11,17,23,29,35,41,47-octasulfo-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene were prepared as described in the literature.[7] Solvents and other chemicals were of analytical grade.

The solubilization experiments and the preparation of the solids were carried out exactly as described in the literature.[1] The C_{60} and γ-CD contents were determined in the solutions by spectrophotometry and polarimetry, respectively, while the water content was measured as drying loss.

UV-vis spectra, as well as second derivative of absorption maxima, were recorded on a Perkin-Elmer Lambda 15 spectrophotometer, while light scattering was investigated with a Brice Phoenix static light scattering photometer. X-ray diffraction experiments were carried out using Cu-Kα radiation ($\lambda = 0.154178$ nm) on a Siemens D500 powder diffractometer system with theta-theta Bragg-Brentano geometry, fixed slits and a pyrolytic graphite secondary monochromator.

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A multimode Topometrix Explorer SPM with a 2.8 µm tube scanner in contact mode was used under ambient conditions in atomic force microscopy. Sample particles dispersed in distilled water were dropped onto glass coverslips. The water was evaporated in dry air. V-shaped silicon nitride cantilevers with a normal spring constant of 0.032 N m^{-1} were used. AFM measurements were carried out over the surface of sample particles.

^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer in a 4 mm ZrO_2 rotor with an MAS rate of 14 kHz at B_0 11.744 T, B_1^H 1.17 mT and B_1^C 4.67 mT field. 128 scans of 2k data points were acquired. The spectrum width is 35 kHz (278 ppm). ^{13}C chemical shifts are reported in δ units relative to an external DSS standard.

To check whether the properties of the solutions and of the solid products depend on their preparation and to obtain information about their stability, freshly prepared and aged solutions (from two weeks up to four years), heated and/or diluted ones, and dried solids (altogether 32 different samples) were prepared and investigated. The amounts of hosts were generally in large excess (in molar ratio 2–20 times, mostly 10 times greater) relative to that of C_{60}. The dissolved and/or precipitated complexes are formed in equilibria; starting with equimolar amounts of the components[1d] proved to be unsuccessful.

Results

UV-vis spectrophotometry

From our own experiments, some UV-vis spectra of different C_{60} solutions of different colours (magenta, yellow or brown) are collected in Fig. 1. It is clear that the maxima of the three strong broad UV bands are shifted to higher wavelengths in the series starting with the cyclohexane solution and ending with aqueous ones prepared with calixarenes **IV** and **VI**. (The last spectrum is practically identical with that of a colloidal C_{60} solution.[5b]) The maximum at $\lambda = 404$–408 nm is a small but very characteristic one, existing only in magenta coloured solutions and missing, or at least covered, in the spectra of the brownish ones.

We have found that the concentration of the fullerene dissolved as the magenta coloured species can be well characterized by the second derivative of this small peak near $\lambda = 407$ nm. After appropriate calibration with benzene solutions, the derivative gives the same concentration as the absorbance at $\lambda = 330$ nm for the magenta solutions, while the former value is always significantly lower (if present) in the case of the brownish or yellow solutions.

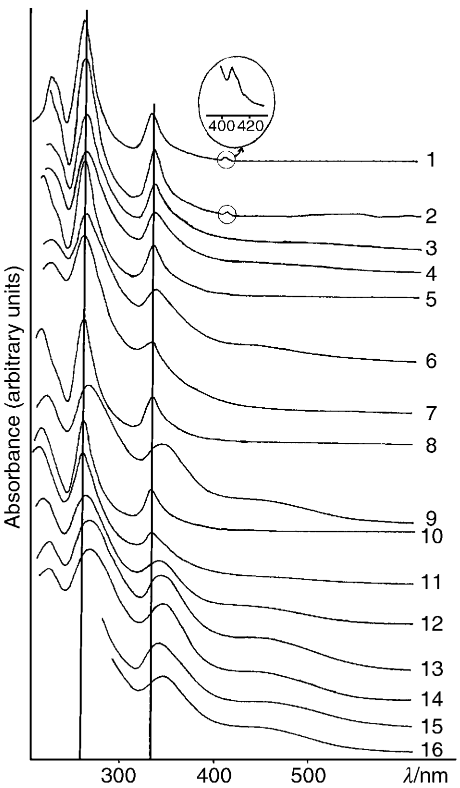


Fig. 1 UV-vis spectra of C_{60}. (**1**): C_{60} in cyclohexane; (**2**–**12**): C_{60} in solutions prepared in different ways, using γ-cyclodextrin; (**2**): stable magenta coloured solution, $c_{CD} = 0.02$ M, $c_{C60} = 2 \times 10^{-4}$ M; (**3**): brownish-yellow, slightly opalescent solution, $c_{CD} = 0.014$ M, $c_{C60} \sim 10^{-4}$ M; (**4**): yellowish-brown, opalescent solution from an originally 1 : 1 mixture, $c_{CD} = 3.4 \times 10^{-3}$ M, $c_{C60} \approx 3 \times 10^{-4}$ M; (**5**): solution **4** after four months, clear yellow, $c_{CD} = 3.4 \times 10^{-3}$ M, $c_{C60} = 10^{-4}$ M; (**6**): yellowish-brown, slightly opalescent solution from an originally 1 : 2 mixture ($c_{CD} = 2 \times 10^{-3}$ M, $c_{C60} \approx 4 \times 10^{-4}$ M) after 2 years; (**7**): the originally magenta solution **2** after 1 year; (**8**): brownish solution (made in cold water) of the 1 : 2 solid complex crystallized in equilibrium with solution **2**; (**9**): solution **8** after 5 min boiling; (**10**): the 1 : 2 complex (see point 8) dissolved in 0.02 M γ-CD, after 5 min boiling; (**11**): a solution of $c_{CD} = 6 \times 10^{-3}$ M (and $c_{C60} \approx 10^{-4}$ M) after 2 h boiling; (**12**): a solution of $c_{CD} = 7 \times 10^{-4}$ M (and $c_{C60} \approx 4 \times 10^{-5}$ M) after 2 h boiling; (**13**): C_{60} solubilized with CD **II**; (**14**): C_{60} solubilized with CD **III**; (**15**): C_{60} solubilized with calixarene **VI**; (**16**): C_{60} solubilized with calixarene **IV**.

Stability and solubility

On storage, the colour of the solutions often changes to deeper brown, but sometimes from brown to magenta. Some of the solutions are stable only for hours, some others can be stored without change for years. The colour change is always accompanied by a solubility change (with the formation of a solid phase). The stability or instability cannot be related to the nature of the preparation, but rather to the CD concentration and to changes in ambient temperature. The solid products are more stable, but they may also undergo some changes (*e.g.*, the originally violet-coloured crystalline powder containing an excess of γ-CD, also turned brown on standing for about six months).

Our experience indicates that the solutions prepared with methylated β-CDs or with cycloisomaltooctaose show the properties of colloidal C_{60}, and are less stable. We tried to use hydroxypropyl-β-CD, too, to complex C_{60}, since hydroxypropylation is known to extend the cavity,[8a] but we failed. Similarly, hydroxypropyl- and trimethyl-γ-CDs (**II** and **III**), proved to be worse complexing agents for C_{60} than γ-CD itself. These CD derivatives produce only less stable brown solutions; their spectra (13 and 14 in Fig. 1) show some similarity to that of colloidal C_{60}, like the calixarenes **VI** and **V**. The solutions prepared using β-CD derivatives, trimethyl-γ-CD (**III**) or calixarene **VI** are completely decomposed in a few months.

We found that the highest achievable concentration of C_{60} in water depends first of all on the degree of dispersity (in the presence of the required amount of complexing agent, of course). Determining the concentration immediately after the dissolution, the highest concentration (1.4×10^{-3} M) can be attained by high-speed vibration milling,[1m] while ball milling gives lower (1.5×10^{-4}–2.5×10^{-4} M) concentrations.[1g]

Over a longer time, precipitation started and the concentration decreased to $\sim 8 \times 10^{-5}$ M (in agreement with the value given in ref. 1(*a*)). Heating the solution for some minutes, a similar effect is induced. (Both the decomposition rate and the effect of heating are highly influenced by the γ-CD concentration: *cf.* spectra 8, 9 and 10 in Fig. 1.) The highest C_{60} concentration in water obtained with calixarene **IV** is 5×10^{-5} M [4] (or 1.5×10^{-4} M, when using high-speed vibration milling[1m]), while the C_{60} concentration in a stable colloidal solution is estimated to be 7×10^{-6} M (although it can be temporarily much higher[5c]).

Light-scattering measurements

Light-scattering measurements showed that all solutions were

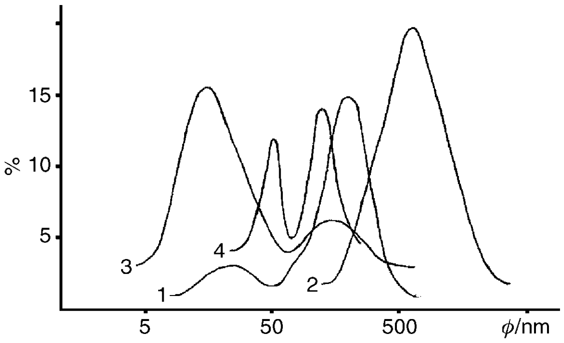


Fig. 2 Particle size distribution in solutions, measured by light-scattering method: (**1**) stable magenta coloured solution (see **2** in Fig. 1); (**2**) solution **1** filtered through a membrane filter of 0.2 µm pores then diluted, after 1 week; (**3**) fresh solution of 1 : 2 mixture of C_{60} and γ-CD prepared by high-speed vibration milling; (**4**) brownish-yellow, slightly opalescent solution (see **3** in Fig. 1), $c_{CD} = 0.014$ M, $c_{C60} \sim 10^{-4}$ M.

heterogeneous (including the apparently clear purple ones, as demonstrated in Fig. 2). The particle size distribution seems to be influenced in the solutions by the original dispersity of the solid phase, because the average diameter of the aggregates was found to be the smallest in solutions prepared by high-speed vibration milling [characterized by mean particle sizes around 15 and 140 nm diameter (in ~4 : 1 ratio, see Fig. 2)]. For a yellowish-brown solution obtained after ball-milling, the mean particle sizes are around 50 and 125 nm (in ~1 : 2 ratio), but this solution had discernible colloidal character, *i.e.* it was opalescent.

The case of a purple solution (prepared by ball-milling and equilibrated for some days) is very interesting, as it contained aggregates of mean particle sizes around 23 and 140 nm diameter (in ~9 : 1 ratio), but the picture changed dramatically when the investigation was repeated after filtration (through a membrane filter of 0.2 µm pores). The second measurement showed aggregates of 600 nm (=0.6 µm!) diameter. Similar phenomena have been found with γ-CD[8b] and with C_{60} itself in different solvents.[9a,b] (A probable explanation is that both C_{60} and γ-CD have non-linear optical properties.)

Chemical analyses

As stated above, equimolar amounts of C_{60} and γ-CD were also kneaded together (after Zhang *et al.*[1d]), but the product was not fully dissolved by water and the spectrum of the aqueous solution showed no special characteristics proving the presence of two different species. Analysing this aqueous solution, the ratio of C_{60} to γ-CD was found to be 1 : 6.7 and most of the C_{60} remained unreacted in the solid. This means that the dissolved species is mainly the 1 : 2 complex and no (soluble?) 1 : 1 complex exists.

The most important results of the chemical analyses are that (i) the filtered and separated solutions always contain γ-CD over the 1 : 2 molar ratio and (ii) the molar ratio of the crystalline phase formed in equilibria in solutions containing an excess of γ-CD is always strictly 1 : 2 [corresponding to the $C_{60}\cdot(\gamma\text{-CD})_2$ formula]. It must be emphasized that the mother liquor was always unsaturated for γ-CD, consequently γ-CD must be complexed in the solid (otherwise it would be dissolved). The water content of the separated solid phases was proved to be 13.5 ± 0.7%.

Powder X-ray diffraction

The chemical uniformity of the last-mentioned solids is also proved by powder X-ray diffraction measurements. Fig. 3 presents the diffraction pattern of a brown solid (molar ratio = 1 : 2, its spectrum is No. 8 in Fig. 1) and those of C_{60} and γ-CD for comparison. As can be seen, the C_{60} and γ-CD form unambiguously a new crystalline phase. This is the clearest proof of the $C_{60}\cdot(\gamma\text{-CD})_2$ supramolecule, since the earlier diffraction patterns always contained some signs of amorphised C_{60}.[1g]

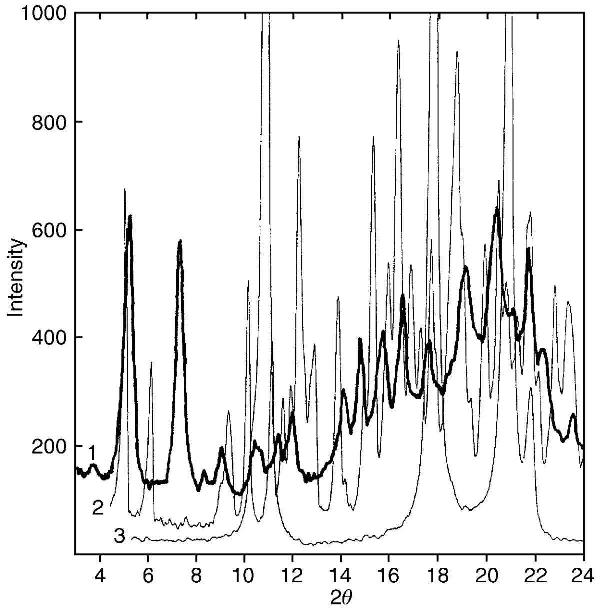


Fig. 3 Powder X-ray diffraction pattern of the 1 : 2 solid brown-coloured complex (**1**), which was crystallized in stable magenta-coloured solution (see **8** in Fig. 1); and those of γ-CD (**2**) and C_{60} (**3**) for comparison.

Atomic force microscopy

Some mgs of the above sample (stored for 14 months) were suspended in water then spread over a sheet of mica and dried at room temperature. This preparation was investigated by atomic force microscopy (which method has never been used previously for this purpose) and the picture of a 1 µm² surface of it is presented in Fig. 4, viewed both from above and in perspective. It can be clearly seen that the solid sample contains rather uniformly sized particles (of ~ 0.1 µm diameter) which appear to be built up of smaller but identical units, confirming the results of the X-ray investigations.

Solid state NMR

The differences found by solid state NMR[6g] between the hydrated and dehydrated species show that hydration has an essential effect on the properties of the $C_{60}\cdot(\gamma\text{-CD})_2$ complex. First these investigations were repeated and it can be established (Fig. 5), that the structure of our hydrated brown species is similar to that of the hydrated violet isomer (ref. 6(*g*)).

To elucidate the effect of water on C_{60} in the solid brown 1 : 2 complex, NMR relaxation time constants were measured in CP/MAS experiments with a set of increasing contact times, τ (Fig. 6). The dynamics of cross-polarization and the connections among the magnetization [$M(t)$] and different parameters can be characterized[9c] by eqns. (1) and (2), where M_0 is a

$$M(t) = (M_0/\lambda)\,[1 - \exp(-\lambda\tau/T_{CH})]\,\exp(-\tau/T_{1\rho}{}^{H}) \quad (1)$$

$$\lambda = 1 + T_{CH}/T_{1\rho}{}^{C} - T_{CH}/T_{1\rho}{}^{H} \quad (2)$$

proportionality constant, T_{CH} is the ^{13}C–^{1}H CP time constant, $T_{1\rho}{}^{C}$ and $T_{1\rho}{}^{H}$ are relaxation times and τ is the ^{13}C–^{1}H CP contact time.

The fitting results are: $\lambda/T_{CH} = 4.86$ ms, $T_{1\rho}{}^{H} = 52.8$ ms. Fig. 7 presents the measured and calculated values [where the solid line is calculated using eqns. (1) and (2)].

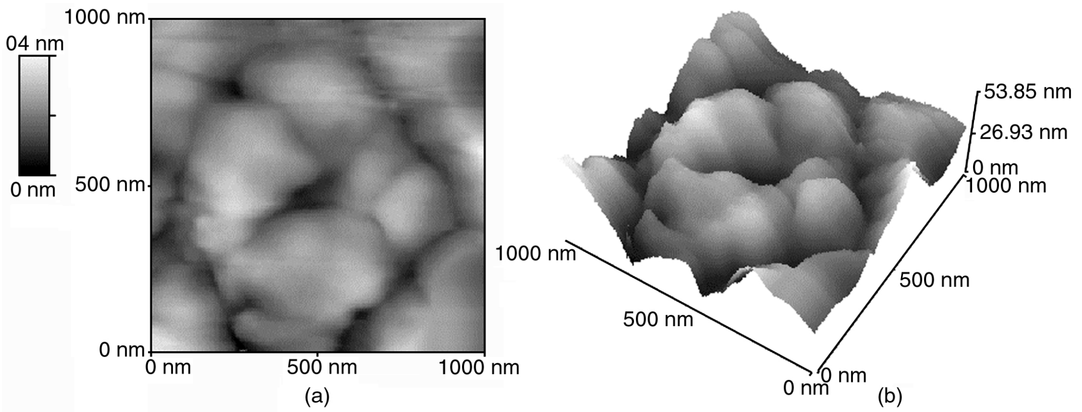


Fig. 4 1000 × 1000 nm height mode image (**a**) of the 1 : 2 solid brown-coloured complex, which was crystallized in stable magenta-coloured solution (see **8** in Fig. 1); and (**b**) 3D image of the identical area (vertical scale drastically differs from the horizontal one).

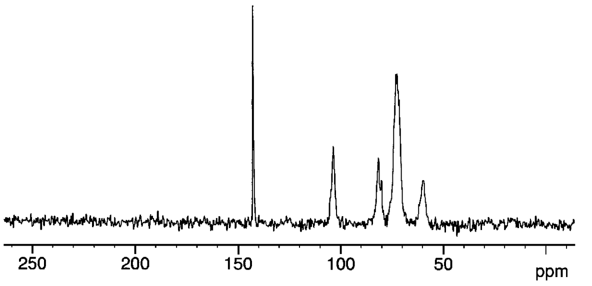


Fig. 5 ^{13}C CP/MAS spectrum of the 1 : 2 solid brown-coloured complex at 11.744 T field, 5 ms contact time and MAS rate of 14 kHz.

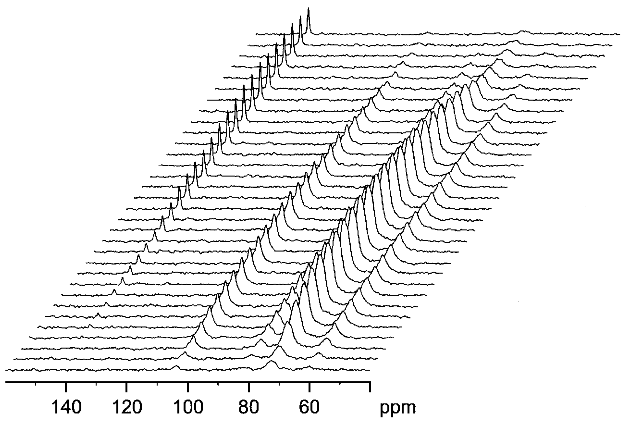


Fig. 6 ^{13}C CP/MAS waterfall NMR spectra of the same sample (see Fig. 5) at 11.744 T field, MAS rate of 14 kHz and contact time in the sets of 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5, 6, 7, 8, 9, 12, 15, 18, 21, 24, 30 and 33 ms.

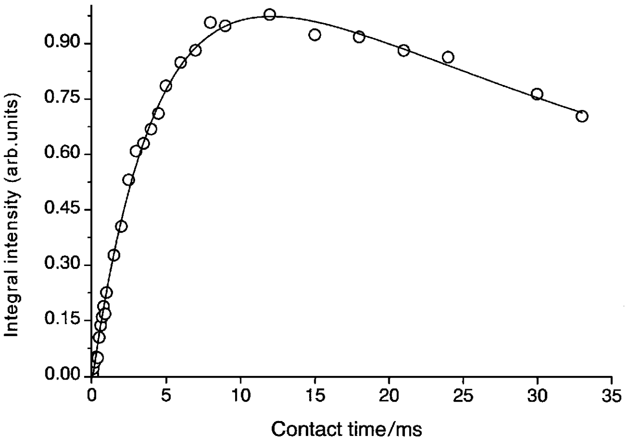
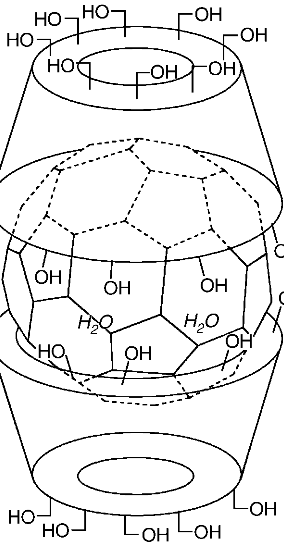


Fig. 7 Normalized integral intensity of the ^{13}C CP/MAS NMR signal *vs.* contact time for C_{60} in the supramolecule at 11.744 T field, MAS rate of 14 kHz, B_1^H 1.17 mT and B_1^C 4.67 mT field.



Scheme 2 Illustration of hydrated C_{60}•(γ-CD)$_2$ complex (relative sizes roughly correct) showing the hydration of both the host and guest molecules.

Discussion

Uniqueness of γ-CD

By comparison of several complexing agents, γ-CD has been shown to be the best host for the solubilization of [60]fullerene. The interaction of C_{60} and γ-CD results in the formation of a C_{60}•(γ-CD)$_2$ inclusion complex, and we proved that the various kinds of preparation recommended in the literature[1] give practically the same product. The 1 : 2 molar ratio is strictly constant in the solid, complexed form, independent of whether it was formed in equilibrium with purple or brown-coloured or perceptibly colloidal solutions. The stable aqueous mixtures have to contain an excess of γ-CD.

The inner diameter of the γ-CD cavity is only 0.95 nm,[8c] while the diameter of C_{60} is estimated to be about 1.0 nm.[9d] Because of this dimensional difference, a complete inclusion is inconceivable, but the secondary hydroxys of the γ-CD rims (see Scheme 2) can be connected by H-bonds (and possibly mediated by water molecules). This way a ditopic host is formed, which makes the supramolecular complex more stable. Both α- and β-CDs could behave similarly but their cavities are too small to accommodate the C_{60} molecule, so it is not surprising that they are unable to form inclusion complexes.[1h,i,6a] Though extending the cavity of γ-CD, the methyl- or hydroxypropyl substituents (hosts **II** and **III**) sterically hinder this type of interaction,[8a] explaining the differences between spectra 2–5 and 13 (Fig. 1).

The uniqueness of underivatized γ-CD is apparent in the UV-vis spectra of C_{60}, which can be almost the same in aqueous γ-CD solution as in cyclohexane[9e] (Fig. 1). A small, but very characteristic, maximum of C_{60} at $\lambda = 404$–408 nm can be observed in solutions made with apolar solvents or with γ-CD in water, but in no other cases. In the spectra of brownish-yellow samples the $\lambda = 440$–640 nm region is more structurised and the absorbances are higher.[4a,9f,g] Significant broadening, red shifts and continuous change in intensity ratios[1e] of the absorption bands can be observed in the spectra of the aged or heated (brown coloured) solutions, as well as in the aqueous C_{60} solutions prepared with other complexing agents.

β-CD and its derivatives, as well as the other macrocycles mentioned, seem to promote the dispersion of C_{60} in water producing a colloidal solution rather than stable soluble complexes (p-Bu^t-calix[8]arene–C_{60} species are formed only in aprotic solvents[4b,c]).

Species existing in the brown solutions. The hydration of C_{60}·(γ-CD)$_2$

The formation of two products has been generally accepted in C_{60}–γ-CD interaction:[1c,i] (i) a complex containing monomeric C_{60} units is of magenta colour with a characteristic peak at $\lambda = 408$ nm (this species has been most thoroughly investigated),[1,3,6] and (ii) another complex, which is yellowish-brown (without the peak at $\lambda = 408$ nm) and is assumed to be a cluster of several C_{60} molecules surrounded by γ-CD molecules. However, the picture of a C_{60} cluster with adsorbed γ-CD molecules does not agree with the analytical data (constant 1 : 2 molar ratio of C_{60} to γ-CD in the crystalline precipitate, independently of whether the solid phase was formed in equilibrium with purple or brown-coloured or perceptibly colloidal solutions, while the mother liquor was always unsaturated for γ-CD), since no strict stoichiometry could exist in such a case.

The contradiction can be solved considering the role of the water in the formation of the C_{60}·(γ-CD)$_2$ complex(es).

The species are surely hydrated in aqueous solution, but the kind of hydration may be different: (i) the (free) hydroxy groups of the γ-CD are bound by H-bridges to water molecules; and (ii) the C_{60} itself can be hydrated (as proved by the relatively long lifetime of aqueous colloidal C_{60} solutions, too).[5]

The solvation of C_{60} takes place in complicated equilibria, which are highly dependent on temperature. It seems that the unusual solute–solvent interactions determining the solubility of C_{60} and its abnormal temperature dependence,[9a,b,h] also play an important role in the characteristics of the spectra. The special interactions are assumed to be the consequence of the multipolar character of the C_{60} molecule: since the electron densities inside the whole molecule are fluctuating very fast,[9g,i] the core of the further supramolecule can be preformed. The best example for this preformation is the preparation of a stable colloidal C_{60} solution by gradual solvation,[5a] where C_{60} is dissolved first in a small amount of benzene, the solution is mixed with a large excess of tetrahydrofuran, then with acetone and finally with water. The C_{60} is first solvated by benzene, which can be replaced by the more polar tetrahydrofuran molecule, *etc.*, ending with the hydrated fullerene producing the stable colloidal solution. Similarly, some complexing hosts (like calixarenes, *etc.*)[1m,2a–d,4a] seem to preform the optimum structure for water substitution, too. [The preparations of C_{60}·(γ-CD)$_2$, starting with organic solvents[1b,f,j,k] may have identical backgrounds.]

The hydrated fullerene is able to form both lower C_{60} aggregates (and in this way stable colloidal solutions) and/or inclusion complexes with γ-CD since the H-bonds between the two hosts[6e] can be sustained *via* the inserted water molecules. The results of ^{13}C NMR experiments on dehydrated and hydrated C_{60}·(γ-CD)$_2$ complexes prove not only the general formation of [C_{60}·(γ-CD)$_2$]·$(H_2O)_x$ species, but also the hydration of C_{60} itself, since the data measured for different C atoms (of C_{60}) are definitely non-equivalent in the two cases. Comparing the curve of Fig. 7 with that in Fig. 4 of ref. 6(*g*), the similarity of the structures of the hydrated violet and brown forms can be established (as well as the dissimilarity to the data of the dehydrated one). Both T_{CH} and $T_{1\rho}^{H}$ values are increased indicating that the flexibility of the complex is enhanced. In the magenta coloured C_{60}·(γ-CD)$_2$·$(H_2O)_x$ species, the water molecules seem to be connected only to the γ-CD domain of the supramolecule, while in the hydrated brown complex the included fullerene is hydrated, too [C_{60}·$(H_2O)_y$·(γ-CD)$_2$·$(H_2O)_z$, as proved by the data of Fig. 7]. Examining Scheme 2, which represents roughly the correct relative sizes, the water molecules hydrating the fullerene can find room between the two γ-CDs.

Since the ^{13}C NMR spectra of the γ-CDs are also different, depending on the presence of C_{60} or C_{60}·$(H_2O)_x$, the properties of these guests (and their inclusion complexes, too) must also be different. As the wavelengths of the C_{60} absorption bands are shifted by solvation, the magenta → brown colour change, as well as the line broadenings in the spectra of the brown C_{60}·(γ-CD)$_2$ solutions, are explained by the different hydrations. As the hydrated fullerene and its γ-CD complex are ready to form higher aggregates, the solutions containing C_{60}·$(H_2O)_y$·(γ-CD)$_2$·$(H_2O)_z$ species are less stable than those with C_{60}·(γ-CD)$_2$·$(H_2O)_x$.

Conclusion

By comparison of several complexing agents and different methods of preparation, we have shown that γ-CD is the best host for solubilization of C_{60}. It produces the most stable solutions of highest concentration, independent of the method of preparation. The primary amorphous product, equilibrated with water, gives crystalline complexes with a reproducible 1 : 2 molar ratio. The uniform crystalline state of the complex is proved by powder X-ray diffraction and atomic force microscopy. Analytical data and solid state NMR indicate that the essentially 1 : 2 complex exists as two different forms: in the violet coloured form, unhydrated C_{60} is included while in the brownish one, C_{60} is also hydrated.

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