Solubilisation of C_{60} in Aqueous Micellar Solution

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There are two states of C_{60} in stable dispersions: molecular and colloidal (mean diameter ca. 10 nm).

In this communication we investigate the properties of C_{60} solubilised in aqueous micellar solutions of Triton X-100 (TX).† Stable dispersions of C_{60} have been obtained and evidence from both UV–VIS spectra and small-angle neutron scattering (SANS) shows that there are two states of C_{60} in these systems, molecular and colloidal (mean diameter ca. 10 nm). A transition from molecular to colloidal C_{60} is induced by increasing the ratio $X = [C_{60}]/[TX]$. At low values of X (ca. 10^{-4}) the UV–VIS spectra are characteristic of monomeric C_{60}, as for conventional hydrocarbon solvents, and no aggregates can be detected by SANS. However, on increasing X (up to 2.52×10^{-3}) we are able to assign the appearance of a new broad band in the UV–VIS spectrum at ca. 440 nm uniquely to the presence of colloidal C_{60} aggregates which have been studied by 'contrast matching' SANS techniques. Both the monomer and aggregate systems remain as stable dispersions over a period of up to 2 weeks.

In typical hydrocarbon solvents C_{60} dissolves as a molecular solution, the solubility is, however, rather low (e.g. saturation concentration in toluene = 2.8 mg cm^{-3}).[1] The absorption spectrum of a solution of C_{60} in toluene has a band at 336 nm and a characteristic sharp peak at 408 nm. Studies of the photochemical and electrochemical properties of fullerenes in solution have been hindered by their rather poor solubility in polar solvents.[1] This proves to be a limiting factor in the study of electron-transfer reactions between the photoexcited triplet state and an electron donor. In a non-polar environment the geminate ion pair is not stabilised by the solvent and back electron transfer takes place rapidly.[2] One way to overcome this problem is to enhance the solubility in water using host molecules such as cyclodextrins[3] of self-assembling structures such as micelles. It has already been shown that C_{60} can be solubilised in aqueous γ-cyclodextrin (cyclomaltooctaose).[3] Within the cavity of the cyclodextrin the fullerene is accessible to reagents dissolved in the solvent, although rates of reaction are reduced.[4] Higher fullerenes such as C_{70} cannot be solubilised in this way. A promising and more versatile method is to use aqueous micellar solutions. It is well known, for example, that pyrene is readily solubilised by SDS micelles, so in principle the micellar environment may be used for C_{60}.‡ Recently there have been reports of C_{60} and C_{70} solubilisation in both micellar and lipid systems.[5–8] However, the preferred location of the fullerenes in the self-assembly systems, and their state of dispersion/solution remains unclear. Hungerbuhler et al. have reported that in aqueous Triton X-100 micelles the absorption spectrum of C_{60} is significantly modified as compared with a pure hydrocarbon environment and attributed this to a specific interaction with the hydrophilic polyethylene oxide moieties with the π-system of the fullerene.[7] The same group also reported that C_{60} could be incorporated in phospholipid vesicles. Again the absorption spectrum is perturbed, and it was proposed that in this system the C_{60} aggregated within the lipid bilayer, accounting for the spectral changes. However, no direct structural evidence has yet been advanced to verify this suggestion. Other groups have not commented upon the state of the lipid-bound fullerenes, although Bensasson et al. have suggested that fullerene aggregates may play an important role in the light-induced electron-transfer reactions of fullerenes across phospholipid bilayers.[8] Here we correlate changes in UV–VIS absorption spectra with the formation of colloidal-sized aggregates of C_{60}.

C_{60} was separated from commercially available carbon soot (Aldrich) by column chromatography on neutral alumina, using hexane–toluene as the eluant. Solutions were prepared in both pure toluene (Aldrich HPLC grade) and absolute ethanol. A stock C_{60} toluene solution was prepared at 2.5 mg cm^{-3}. Triton X-100 (Aldrich) and Triton X-100-Reduced (Sigma) were used as received. A concentrate was prepared by quantitatively mixing neat Triton-X100 and the stock fullerene toluene solution. Following rotary evaporation (Buchi) of the toluene at 40 °C a C_{60}-rich transparent yellow–brown oil resulted, which was dissolved in water to produce the final solution. A number of samples were made at various values of X; the concentrate was then diluted in water as required. An alternative preparative method is to add an aliquot of a C_{60} toluene solution to TX in water. Initially an opaque emulsion is formed; however, when this is left to stand in the dark at room temperature for ca. 12 h the evaporation of toluene results in a transparent stable micellar dispersion. The spectral properties of samples were independent of the method of preparation. By using the reduced form of Triton X-100 (Sigma) UV–VIS spectroscopy indicates that following either of these procedures there is no residual toluene in the final dispersions (lower limit of detection of toluene = 5×10^{-5} mol dm^{-3}). All experiments were performed at 25 °C.

Initial investigations of the spectra of monomeric and aggregated C_{60} were carried out in pure toluene and ethanol (monomer) and mixtures of the two solvents (aggregates). The UV–VIS absorption spectrum of C_{60} in toluene solution is shown in Fig. 1(a). The spectrum in ethanol [Fig. 1(b)] has a virtually identical profile, although is much weaker owing to
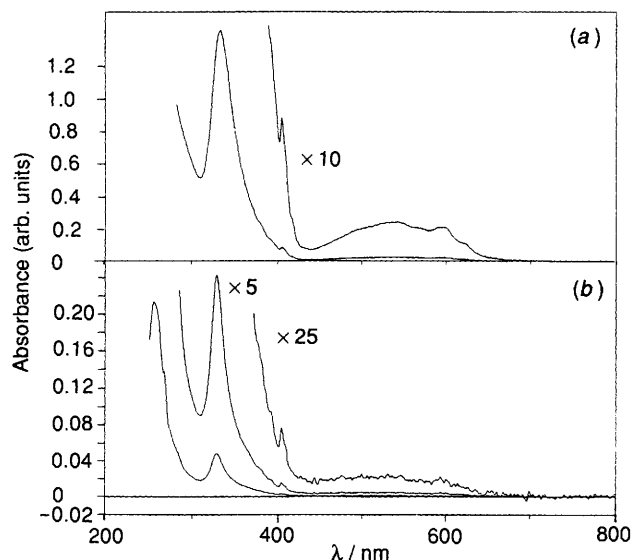

Fig. 1 Absorption spectra of C_{60} in (a) toluene and (b) ethanol

the very low solubility of C_{60} in this solvent.[1] The band at 336 nm in toluene has been blue-shifted by 8 nm and the spike moved to 405 nm. This observation contradicts the previous report in which it was claimed that in alcohols the spectrum was perturbed by the interaction of the fullerene π-system with the polar solvent.[7] Addition of a small amount of a toluene solution of C_{60} to an excess of ethanol gives a similar spectrum. As the amount of added fullerene rises to the solubility limit in ethanol, the solution becomes pale-yellow. The absorption spectrum of this shows the presence of a new band at ca. 440 nm, the broadening of the band at 330 nm and a reduction in the relative intensity of the spike at 403 nm. Filtration of this mixture through a 0.2 µm filter yields a mustard-coloured residue and clear solution, with an absorption spectrum similar to that observed in ethanol, but showing a small difference at ca 440 nm. This is attributed to a small amount of C_{60} aggregate which has passed through the filter (i.e. diameter <200 nm). The two spectra and the difference spectrum are shown in Fig. 2. The difference spectrum [Fig. 2(c)] is then expected to be representative of the aggregates only, and clearly resembles the absorption spectrum of an evaporated film of C_{60} reported by Hebard et al.[9] More specifically, there is band broadening, the appearance of a new band at ca. 440 nm and the absence of the spike at ca. 405 nm. The yellow colouration observed these solutions is therefore due to the formation of small particles or aggregates of C_{60} and the optical properties of these aggregates are quite distinct from those of the monomeric, solvated material.

The UV–VIS absorption spectra of aqueous micellar solutions of C_{60} at two different values of X are shown in Fig. 3. For $X = 3.22 \times 10^{-4}$ [Fig. 3(a)] the spectrum closely resembles that of monomer C_{60} [Fig. 1(a)] with a sharp peak at 335 nm, a spike at 405 nm and only a very weak absorption band at ca. 440 nm, inferring that occupied micelles contain only monomeric C_{60}. When X is increased by a factor of 4 significant spectral changes are obvious [Fig. 3(b)]. The peak at 335 nm broadens and there is growth of a band at ca. 440 nm, attributed to colloidal aggregates [<200 nm diameter, see Fig. 2(b)]. It is clear that as the concentration of C_{60} is increased relative to TX there is a tendency for aggregation to occur, producing a solution with the absorption spectra of a thin film of solid material.[9] It was possible to recover C_{60} from the monomeric and aggregated micellar solutions by extraction with toluene. The recovered fullerene is unchanged, having the characteristic spectral signature of C_{60}. Furthermore, there was no evidence of a spike at 424 nm which would indicate the presence of $C_{60}O$.[10]
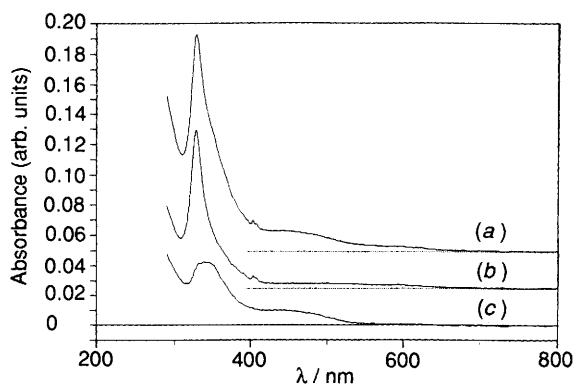
In order to study the size of these C_{60} aggregates we have performed a series of SANS experiments using the LOQ instrument on the pulsed ISIS source at the SERC Rutherford Appleton Laboratory UK.[11] By varying the ratio $H_2O : D_2O$ it is possible to 'contrast match'[12] the aqueous phase to either TX or C_{60}. For example a mixture 83% H_2O and 17% D_2O completely 'contrast matches' the scattering from TX, making the micellar scattering disappear. In this way we have been able to measure the SANS exclusively from the C_{60}. Fig. 4 shows the SANS from C_{60} aggregates, with $X = 2.52 \times 10^{-3}$. The absolute scattering cross-section is entirely consistent with C_{60} particles at the bulk density of 1.65 g cm^{-3}, indicating that the colloidal C_{60} contains an insignificant amount of surfactant. This result suggests the absence of a surfactant monolayer coating the C_{60} particles. Varying the $H_2O : D_2O$ ratio supports this conclusion. The solid line fit to the data was obtained using a Schultz distribution of spheres, shown inset, of mean diameter ca. 10 nm (i.e. ca. 90 C_{60} molecules on average) and a relative high polydispersity of 75%. Similar fits might be obtained assuming ellipsoidal particles, but owing to the broad polydispersity it is not possible unambiguously to assign a shape to the aggregates. These SANS data are not sensitive to the presence of C_{60} monomers or particles much larger than ca. 100 nm. When X is decreased to ca. 8×10^{-5}
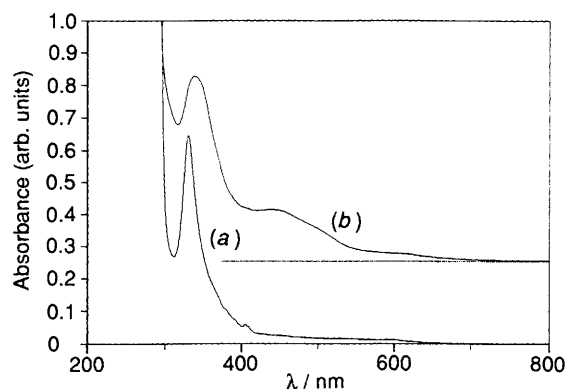
Fig. 3 Absorption spectra of C_{60} in aqueous micellar solutions of Triton-X100 at different values of X (see text). $X = (a)\ 8.13 \times 10^{-5}$ and $(b)\ 3.22 \times 10^{-4}$.

Fig. 2 Absorption spectra of C_{60}: (a) yellow solution prepared by addition of toluene solution to an excess of ethanol, (b) the filtrate after passage through 0.2 µm filter and (c) the calculated difference spectrum. Note that in (b) there is still evidence of aggregate at 450 nm, assumed to be caused by particles of diameter $D < 200$ nm.
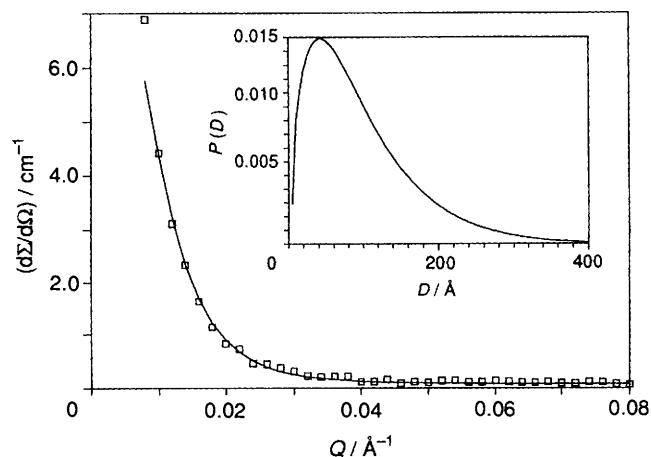
Fig. 4 SANS profile for C_{60} aggregates $X = 2.52 \times 10^{-3}$. Intensity in absolute cross-section units $d\Sigma/d\Omega$ as a function of momentum transfer Q. Solid line is fit for a Schultz distribution of polydisperse spheres. Inset probability function $P(D)$, D particle diameter.

this SANS signal disappears, as would be expected if C_{60} were molecularly dispersed. It is important to note that a control sample, in which [$^2H_8$]toluene was evaporated out of a TX micellar solution demonstrated that the SANS was not related to any residual toluene left in the preparation.

Under carefully controlled conditions it is possible to prepare micellar solutions of C_{60} using Triton-X100 surfactant. The C_{60} may be present either as monomer or colloidal aggregates depending on the molar ratio $X = [C_{60}]/[TX]$; increasing X induces aggregation. Preliminary studies have shown that the photochemistry of the two systems is different; in aerated solutions the monomeric C_{60} is an efficient sensitiser of singlet oxygen ($\Phi_A = 0.8 \pm 0.2$), whilst irradiation of the aggregated form produced no detectable singlet oxygen.§ Further photochemical studies are underway and will be reported at a later date.

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Footnotes

† Triton X-100 is a non-ionic surfactant, $(CH_3)_3CCH_2C(CH_3)_2$-$C_6H_4O(CH_2CH_2O)_nH$, where $n = 8$–10. The alkyl and poly-ethyleneglycol chains are in the 1,4 positions of the aromatic ring. It has a cmc of 2.4×10^{-4} mol dm^{-3}, forming micelles with an aggregation number of ca. 140.

‡ Attempts at using SDS for dispersing C_{60} gave the aggregated from only. These experiments will be reported at a later date.

§ Singlet oxygen was measured by the time-resolved luminescence at 1270 nm, following 355 nm excitation. The observed lifetime in H_2O was 4.0 μs, and the quantum yield was determined relative to Rose Bengal ($\Phi_A = 0.75$).[13]

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