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Stable Dispersions of Fullerenes, C₆₀ and C₇₀, in Water. Preparation and Characterization

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Stable aqueous dispersions of fullerenes, C₆₀ and C₇₀, were prepared by simply injecting into water a saturated solution of fullerene in tetrahydrofuran (THF), followed by THF removal by purging gaseous nitrogen. To our knowledge, this is the first report of the stable dispersion of C₇₀ in water. Fullerenes are dispersed as monodisperse clusters in water, 60 nm in diameter. High resolution transmission electron microscopy revealed the polycrystalline nature of the cluster. The preparation of the dispersion is very easy to perform, and the dispersions thus obtained are of excellent colloidal stability even though no stabilizing agent is used. It was found that the surface of the cluster is negatively charged and the electrostatic repulsion between the negatively charged cluster surfaces is important for the stability of the dispersions.

Introduction

Interesting biological activities of water-soluble fullerene derivatives have been discovered,^{1–4} and there has been increasing interest in preparation of aqueous solutions of fullerenes.^{1–8} As fullerenes themselves are virtually insoluble in water,⁹ this has been achieved by chemical modification of fullerenes,^{1–4} formation of water-soluble host–guest complexes,^{5–7} or solubilization by surfactants.^{6–8}

While a true molecular solution of fullerenes in pure water cannot be prepared, there have been some attempts to disperse fullerenes stably in water without any stabilizer.^{10–13} Scrivens et al. dissolved C₆₀ in benzene and diluted the solution first with tetrahydrofuran (THF), then with acetone, and finally with water. They obtained an aqueous dispersion of C₆₀ after distilling out organic solvents.¹⁰ In another attempt, sonication was applied to a mixture of a solution of C₆₀ in toluene and water for several hours until the evaporation of toluene was completed. C₆₀ did not precipitate as toluene was removed,

but a stable colloidal dispersion of C₆₀ in water was obtained instead.^{11–13} These preparation methods are very simple and make it possible to evaluate the biological activities of unmodified fullerenes.¹⁰ However, in these attempts, fullerenes are first dissolved in a highly toxic organic solvent such as benzene or toluene. For biological study or medical applications, these solvents should be eliminated from the preparation process, and a new procedure has to be developed for these purposes.

To study the biological activities of the colloidal fullerene, it is essential to know the fundamental properties of the fullerene dispersion such as structure and size distribution of the colloidal fullerene particles and mechanism of the stabilization. The biological activities of the colloidal fullerene might be different from those of water-soluble fullerene derivatives^{1–4} or fullerenes solubilized in water via complexation^{5–7} or with the aid of a surfactant.^{6–8} However, even these fundamental properties of the dispersions still remain to be clarified. The stable dispersion of a pure carbon allotrope, fullerene, in water without any stabilizing agent is also intriguing from the viewpoint of colloid science.

This paper describes a new preparation procedure for stable dispersions of fullerenes, C₆₀ and C₇₀, in water using a relatively nontoxic solvent, THF. The structure and size distribution of the colloidal fullerene clusters are studied in detail. The stabilization mechanisms of the fullerene dispersions are also discussed.

Experimental Section

Materials. C₆₀ (>99.9% pure) and C₇₀ (>98% pure) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and used as received. THF was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and distilled once just before use. Millipore water was used throughout the work (Millipore, Bedford, MA). Care was taken to minimize exposure of the samples to light during the experiments.

Sample Preparation. Freshly distilled THF was deaerated by purging gaseous nitrogen for at least 30 min. A small amount of solid C₆₀ or C₇₀ and THF (20 cm³) were placed in a vial with a screw cap and stirred overnight under argon atmosphere at room temperature. Excess solid was filtered off with a PTFE membrane filter (nominal pore size 0.45 μm, Acrodisc, Gelman, Ann Arbor, MI) to give a saturated solution of C₆₀ or C₇₀ in THF. The solubility of fullerenes in THF, measured spectrophotometrically as described below, was found to be 1.3 × 10^{−5} mol dm^{−3} and 2.7 × 10^{−5} mol dm^{−3} for C₆₀ and C₇₀, respectively. C₆₀

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was once reported to be insoluble in THF,⁹ but our result is reproducible and C₆₀ is certainly soluble in THF. The solution of C₆₀ (2 cm³) was injected into an equal amount of water in a test tube, and gaseous nitrogen was purged through the solution at a flow rate of 0.2 dm³ min⁻¹ for at least 1.5 h to remove THF. During the nitrogen purge, the test tube was immersed in a water bath to prevent the solution from being cooled by THF evaporation. A part of water also evaporated, and this was compensated by adding water up to the original volume. A yellow and visually clear solution formed after THF removal. More than 75% of C₆₀ remained in water, while the rest formed a thin yellow film on the inner wall of the test tube. Sample solutions of C₇₀ in water were prepared by the same procedure. A simple mixture of water and THF was processed in the same way, and the completeness of the THF removal was checked by analyzing the THF concentration by gas chromatography. It was found that the amount of residual THF was less than the detection limit of the apparatus (<1 ppm).

The solutions of C₆₀ and C₇₀ in THF are apparently stable upon storage under argon atmosphere in the dark. However, if THF is not distilled, the color of the C₆₀ solution turns from faint magenta to yellow, which probably results from reaction with an impurity in THF such as peroxide.¹⁴

Concentration Determination. The concentration of fullerenes in THF was determined by measuring the absorbance at 330 nm for C₆₀ or at 331 nm for C₇₀. The reported absorption coefficients (ϵ) at 328 nm for C₆₀ ($\log \epsilon = 4.71$) and at 330 nm for C₇₀ ($\log \epsilon = 4.38$) in *n*-hexane¹⁴ were used for the calculation. The concentration of fullerenes in water was estimated as follows. A fullerene dispersion in water (1 cm³) and 2% NaCl solution (1 cm³) were mixed, and toluene (2 cm³) was added. The mixture was sonicated for a few minutes and was set in the dark until the aqueous and toluene phases separated. The upper toluene phase was withdrawn carefully, and the absorbance at 334 nm for C₆₀ or at 335 nm for C₇₀ was measured. The absorption coefficient in *n*-hexane was used for calculating the concentration, although the absorption spectra of C₆₀ and C₇₀ in toluene show a red shift by 4 nm compared with those in *n*-hexane. No absorption due to fullerenes was observed in the aqueous phase.

Spectroscopic Measurements. UV–visible absorption spectra were recorded on a Shimadzu UV-2400PC UV–vis recording spectrophotometer (Shimadzu, Kyoto, Japan). All the spectra reported here are background corrected. All the measurements were done at room temperature.

Transmission Electron Microscopic (TEM) Observations. Specimens for TEM observations were prepared by depositing 4 mm³ of the sample solution on a 150-mesh copper grid, coated with a collodion film and deposited by carbon. The specimens were air-dried in the dark and stained by exposure to 4% OsO₄ vapor for 30 min, followed by extensive washing with pure water and drying in vacuo. The specimens were examined on a JEOL JEM-1210 (JEOL, Japan) operating at 120 kV incident beam energy. The specimens for high-resolution TEM (HRTEM) observations were prepared in the same manner, but were not stained. HRTEM observations were performed at Nissan-Arc, Ltd. (Yokosuka, Japan) with a Hitachi H-9000UHR (Hitachi, Japan) operating at 300 kV incident beam energy.

Dynamic Light Scattering (DLS) Measurements. The size distribution of the fullerene clusters was studied by DLS. DLS measurements were performed on a DLS-820 light scattering system (Otsuka electronics Co., Ltd., Osaka, Japan) equipped with He–Ne laser at 25 °C. A detailed description of the apparatus can be found elsewhere.¹⁵

HPLC Analysis. HPLC analysis of fullerenes was carried out on a Waters LC Module 1 equipped with a TSK-Gel ODS-125T (Tosoh, Japan). *n*-Hexane was used as a mobile phase. Fullerenes were detected by the absorbance at 350 nm.

Results

Spectroscopic Study. As soon as a faint magenta solution of C₆₀ in THF was injected into water, a yellow

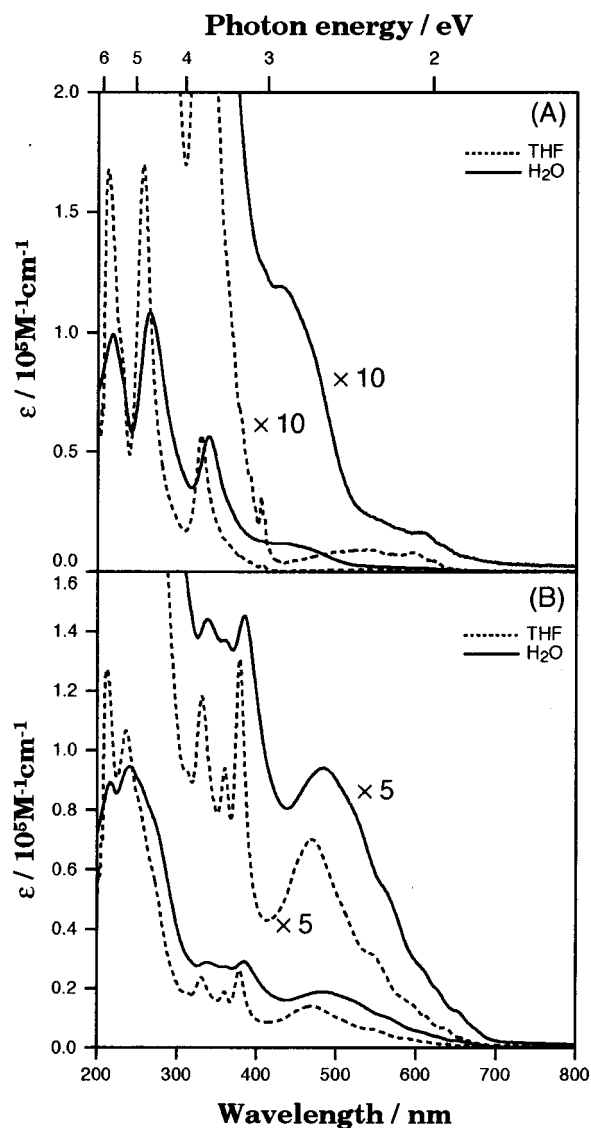


Figure 1. UV–visible absorption spectra of C₆₀ (A) and C₇₀ (B) in THF (broken line) and water (solid line). Inserts are the same spectra at the magnifications indicated. The measured spectra were normalized by the fullerene concentration for comparison of the spectra in THF and water. The C₆₀ concentrations are 1.3×10^{-5} mol dm⁻³ in THF and 1.0×10^{-5} mol dm⁻³ in water. The C₇₀ concentrations are 2.7×10^{-5} mol dm⁻³ in THF and 2.0×10^{-5} mol dm⁻³ in water.

and visually clear solution formed. The color remained the same even after THF removal. A color change from orange to pinkish purple was also observed for C₇₀. UV–visible absorption spectra of C₆₀ and C₇₀ in THF and water are shown in Figure 1. In THF, both C₆₀ and C₇₀ show the typical absorption spectra in solution. Peak positions and relative peak intensities are in good agreement with the reported spectra of C₆₀ in *n*-hexane¹⁶ or C₇₀ in Decalin.¹⁷

In water, the three strong absorption peaks of C₆₀ in the UV region show red shifts from 213 to 218 nm, from 257 to 265 nm, and from 330 to 339 nm, respectively. The peaks are also broader and less intense. The intensity reduction is larger for the absorption at shorter wavelength. The spectra show even larger differences in the

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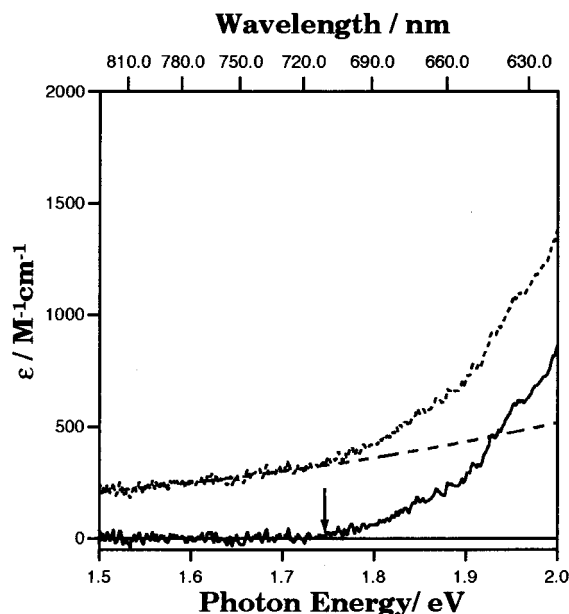


Figure 2. Part of the absorption spectra of C_{60} in water close to the absorption edge. The dotted line shows the measured spectra, while the broken line shows the best fit of scattering to the measured spectra according to Rayleigh scattering law. Solid line shows the spectra after scattering correction. The arrow indicates the onset of the absorption.

visible region as is expected from the color change of the solution. The sharp spike at 405 nm completely disappears, and a new broad absorption between 420 and 520 nm appears. The spectra of C_{60} in water, especially the new broad band between 420 and 520 nm, closely resemble those of a solid thin film.¹⁸ The spectroscopic results strongly suggest that C_{60} is not dissolved in water molecularly, but is dispersed as fine solid clusters. Figure 2 shows a part of the absorption spectra of C_{60} in water near the absorption edge. The weak absorption at low energy region is ascribed presumably to scattering, as it follows Rayleigh scattering law; i.e., the intensity is proportional to $1/\lambda^4$, where λ is the wavelength. The scattering contribution was negated by subtracting the computationally generated scattering contribution from the measured spectra. The absorption of C_{60} in water starts at 1.75 eV. The absorption of pristine solid C_{60} starts between 1.5 and 1.7 eV.^{19,20} The blue shift of the absorption edge indicates that C_{60} forms clathrate crystals, instead of pristine crystals, in water.¹⁹

The spectra of C_{70} also change from the typical solution spectra in THF to the spectra of a solid thin film²¹ in water. The blue shift of the absorption edge from 1.25 eV in pristine C_{70} ²¹ to 1.69 eV in water is also observed.

Characterization of Fullerene Dispersions. TEM micrographs of the C_{60} and C_{70} dispersions are shown in Figure 3. Clusters, fairly monodisperse in size, are observed in an aggregated state. The size of the individual cluster agrees well with the average hydrodynamic diameter obtained by DLS (62.8 nm for C_{60} and 63.0 nm for C_{70}), and is significantly smaller than the values reported previously for fullerene dispersions in water.^{10,11} The aggregation would have taken place in the specimen

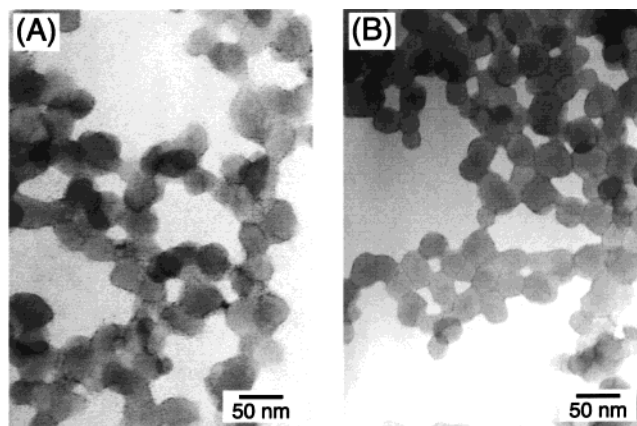


Figure 3. TEM micrographs showing the C_{60} clusters (A) and C_{70} clusters (B) in an aggregated state. The aggregation would have taken place in the specimen preparation process, most probably during drying.

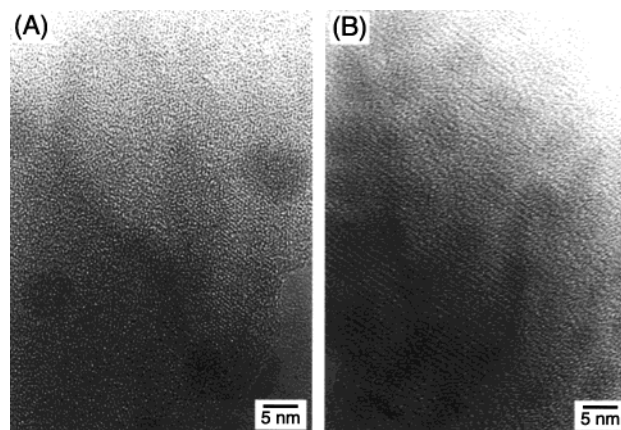


Figure 4. HRTEM micrographs of a C_{60} cluster (A) and a C_{70} cluster (B).

preparation process, most probably during drying. DLS results also indicate the narrow size distribution of the clusters. Typical HRTEM pictures of the fullerene cluster are shown in Figure 4. The pictures clearly show that both C_{60} and C_{70} clusters are polycrystalline in nature. The polycrystalline structure is most clearly seen in the bottom right part of the C_{60} picture (Figure 4A). This part shows a domain close to the periphery of a C_{60} cluster, and is supposedly most free from the confusion due to the projection of overlapping structures.

HPLC analysis of fullerenes, recovered by lyophilizing the aqueous dispersion, did not show any evidence of fullerene degradation such as oxide formation.¹⁰

Colloidal Stability of the Dispersions. Surprisingly, the dispersions of C_{60} and C_{70} thus prepared are very stable, and no precipitation was observed even after long storage in the dark at room temperature (at least 9 months after preparation). Absorption spectra of the C_{60} dispersion measured immediately after preparation and after storage for 1 month at room temperature in the dark were indistinguishable. The size of the cluster, measured by DLS, also did not change during storage. Dialysis of the dispersion against pure water did not affect the stability or size of the cluster, ruling out any possible stabilizing effect of residual THF.

The stability is, however, significantly affected by salt addition. Figure 5 shows the absorption spectra of the C_{60} dispersion in water with and without 1% NaCl. The spectra in the presence of NaCl show a red shift of 5 nm. The absorption below 286 nm becomes weaker, while the

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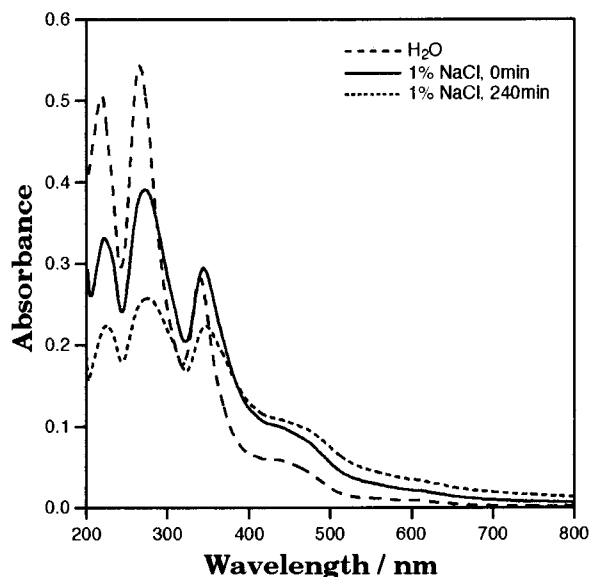


Figure 5. UV-visible absorption spectra of C_{60} in water (broken line) and in 1% NaCl measured immediately after NaCl addition (solid line). The C_{60} dispersion in 1% NaCl was prepared by diluting the dispersion in pure water twice with 2% NaCl solution. Also shown are the spectra of the same sample measured in 4 h after NaCl addition (dotted line). The upturn observed below 210 nm in the spectra with NaCl is an artifact due to incomplete background correction because NaCl has strong absorption below 245 nm. The C_{60} concentration is 5.0×10^{-6} mol dm^{-3} .

absorption above 286 nm becomes stronger. Evolution of turbidity is also apparent from the increased absorption at longer wavelength. Shown together are the absorption spectra measured in 4 h after NaCl addition. The spectral intensity decreased dramatically as a function of time, and C_{60} eventually precipitated at the bottom of the container as yellow sediment. In addition, if 1% NaCl solution was used for the dispersion preparation, instead of pure water, a similar yellow and clear solution was obtained when a solution of C_{60} in THF was injected, but C_{60} formed a yellow film on the inner surface of the test tube wall during THF removal, and did not remain at all in water.

These observations lead us to conclude that electrostatic repulsion would be important for the stability of the dispersions. Indeed, preliminary electrophoretic light scattering measurements (ELS-8000, Otsuka Electronics, Osaka, Japan) revealed that the C_{60} clusters are negatively charged (ζ -potential ~ -30 mV). The result agrees with the previously reported result for colloidal C_{60} in water, although Mchedlov-Petrosyan et al. found a much smaller ζ -potential (-9 mV).¹² Electrostatic repulsion between the negatively charged cluster surfaces plays an essential role in the stabilization of the fullerene clusters in water.

Properties of the Fullerene Dispersions. It was not possible to extract fullerenes from a solution in toluene to water. However, it was also not possible to extract fullerenes from a dispersion in water to toluene. Similar results have been reported for other C_{60} aqueous dispersion systems.^{10,11} By contrast, C_{60} , dissolved in water via complexation with γ -cyclodextrin, was extracted to toluene.^{5,22} In the case of C_{60} incorporated into artificial lipid membranes, C_{60} was not extracted to toluene, but the extraction became possible once the vesicle was destructed by adding KCl.⁸ Addition of KCl was also required to

extract PVP-solubilized C_{60} to toluene.⁶ The same holds for the present system. When NaCl was added to the dispersion, C_{60} and C_{70} were extracted into toluene, and the toluene phase exhibited faint magenta or orange, characteristic colors for a solution of C_{60} or C_{70} in toluene, respectively. This makes it possible to measure the fullerene concentration in water spectrophotometrically, as described in the Experimental Section.

As the fullerene dispersions in water were prepared with a saturated solution in THF, it is impossible to prepare the dispersion with higher fullerene concentrations. However, by injecting a saturated solution in THF into the dispersion of fullerenes prepared beforehand, it is possible to concentrate fullerenes in water. When C_{60} was concentrated twice in water in this manner, scattered light intensity increased almost twice, but the size remained the same by DLS and TEM. This means that the C_{60} clusters do not grow in size by further feed of C_{60} , but new clusters of the same size are formed instead. By this procedure, we were able to concentrate the dispersion 4 times without any problem.

Discussion

Considering the sample preparation procedure we employed, the formation of polycrystalline clusters of fullerenes in water is no surprise.^{23,24} However, the stability of the dispersions of fullerenes, which are pure carbon allotropes, deserves discussion. The extraordinarily high stability of the fullerene dispersion in water seems to be achieved by the negatively charged surface of the clusters. The negatively charged cluster surface is one of the possible reasons why fullerenes cannot be extracted from the aqueous dispersion to toluene. The results obtained by the C_{60} concentration experiments that the C_{60} clusters do not grow by further addition of C_{60} could also be explained by the same reason.

The origin of the negative charge on the fullerene cluster surface is, however, not clear at present. Chemical modification can be ruled out based on the results of the toluene extraction experiments and HPLC analysis. The negative charge might simply come from adsorption of hydroxyl ions, which has been observed for hydrophobic surfaces in water.^{25–27} However, the ζ -potential of the comparable magnitude was also observed for the fullerene clusters formed in polar organic solvents,¹⁵ and it seems difficult to explain the negative charge solely by this mechanism.

Possible other mechanisms include clathrate formation and charge transfer. On one hand, fullerenes are known to form clathrate crystals with simple organic solvent molecules such as *n*-pentane, diethyl ether, and 1,3-dibromopropane.^{19,28} Clathrate formation of a C_{60} derivative with THF has also been reported.²⁹ These clathrate crystals were grown from a toluene solution by the precipitation method, and this is basically the same procedure as we employed to prepare the dispersions in

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water. Thus, it is likely that fullerenes also form clathrate crystals, instead of pristine crystals, in water, as is suggested by the absorption edge analysis. The most probable guest is THF, but formation of hydrated crystals of fullerenes cannot be neglected.¹³

On the other hand, fullerenes are strong electron acceptors (electron affinity = 2.7 eV for both C₆₀ and C₇₀²⁰). For the C₆₀- γ -cyclodextrin complex, Yoshida et al. reported that there exists charge transfer between C₆₀ and γ -cyclodextrin, with ether oxygen and alcoholic oxygen being electron donors.³⁰ The same charge transfer would take place in the clathrate crystals of fullerenes in water, with the ether oxygen of THF or the alcoholic oxygen of water being an electron donor. These mechanisms would also be responsible for the negative charge of the fullerene clusters, in addition to hydroxyl ion adsorption. Further study of the cluster structure or detailed electrokinetic experiments would make these points clear.

Besides the dispersions in water, there are some reports regarding fullerene aggregates in organic solvents or organic solvent mixtures including ours.^{15,31–33} Formation of the fullerene aggregate is also reported in pyridine/water mixtures.³⁴ The cluster formation itself would be a

general property of fullerenes, although the details such as the size of the cluster depend on the choice of the solvent.

Conclusion

Fullerenes, C₆₀ and C₇₀, are dispersed in water as fine clusters. To our knowledge, this is the first report of the stable dispersion of C₇₀ in water. The clusters are polycrystalline, and very possibly clathrate crystals. The dispersions are very stable even though no stabilizer is used. It was found that the surface of the cluster is negatively charged and the electrostatic repulsion between the negatively charged cluster surfaces is important for the stability of the dispersions.

As our procedure is easy to perform and does not use toxic organic solvents such as benzene or toluene, the dispersions thus prepared seem suitable for biological uses or medical applications, and would contribute significantly to the study of biological activities of fullerenes. The dispersion could also be applied to other water-based applications such as those in food or cosmetics.

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