10460 *J. Am. Chem. Soc.* **2001,** *123,* 10460−10467

Stable Colloidal Dispersions of Fullerenes in Polar Organic Solvents

Rossitza G. Alargova,* Shigeru Deguchi, and Kaoru Tsujii

Contribution from the DEEPSTAR Group, Japan Marine Science and Technology Center,
2-15 Natsushima-cho, Yokosuka 237-0061, Japan

Received January 23, 2001. Revised Manuscript Received May 15, 2001

Abstract: Colloidal dispersions of C_{60} and C_{70} were prepared by simply mixing a fullerene solution in a good solvent with a poor polar organic solvent for fullerenes. The process was very easy and fast and the formation of particles with average diameter in the colloidal range was detected immediately after the components were mixed. The formation and the properties of the fullerene particles were studied mainly with dynamic light scattering and high-resolution transmission electron microscopy. The most interesting findings are the long-term colloid stability of the samples in the absence of any stabilizers, the relatively narrow size distribution, and the different average sizes of the particles formed by C_{60}, C_{70}, and their mixtures. The influence of various factors such as fullerene concentration, mixing procedure, solvent properties, and C_{60}/C_{70} ratio was investigated. It is shown that the smaller particles are formed when the total fullerene concentration in the good solvent is decreased and that the fullerene particles have crystalline structure. The measured negative values for the electrophoretic mobility of the particles suggest that fullerene dispersions in polar organic solvents are stabilized by repulsive electrostatic interactions.

Introduction

Fullerenes and carbon nanotubes are currently of great interest in many areas of science and technology due to their unique chemical and physical properties.[1−3] Many studies and patents have appeared suggesting applications of fullerenes as optical and electronics materials, superconductors, sensors, building blocks for new chemicals and materials, optical limiters and light emitters, etc.[1,4] However, many of the potential applications are hindered because the fullerenes are not soluble or sparingly soluble in many solvents.[1,3,5] Hence, looking for the possibilities to increase the solubility of C_{60} and other fullerenes in such solvents as water and polar organic liquids is of particular interest. Fullerenes interact with solvents in interesting ways that could provide useful information about the mechanism of solute−solvent interactions. It has been shown that there is no single solvent parameter that predicts in general the solubility of C_{60} and that usually it dissolves in a solvent that has a large refractive index, a dielectric constant around 3−4, a large molecular volume, and a tendency to act as a moderate nucleophile.[1,5] An interesting observation is the anomaly in the solubility of C_{60} as a function of temperature.[6,7] Recently, many efforts have been made to find a way to dissolve fullerene molecules in water for possible use in biology and medicine. In most cases water-soluble fullerene derivatives[8−12] have been synthesized, or fullerenes have been included in some water-soluble complexes.[13,14] Combinations of solvents intended to increase gradually the polarity of the medium[15,16] and emulsifying a toluene solution of C_{60} in water by means of ultrasound followed by the removal of toluene[17,18] have also been tried. The solubility of fullerenes in some organic solvents has been increased by grafting fullerene molecules with polymer chains,[19−21] or by solubilization and encapsulation of fullerenes by amphiphilic block copolymers.[22,23] Most of these studies show that the fullerenes and their derivatives are dispersed in the polar media in the form of aggregates.[9,12−19,22,23] The unusual solvatochromism of C_{70} and C_{60} observed at high volume

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* To whom correspondence should be addressed: fax +81−468−66−6364; e-mail rossitza@jamstec.go.jp.

(1) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, CA, 1996.

(2) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685−693.

(3) Shinohara, H.; Sato, Y. *Chemistry and Physics of Fullerenes*; Nagoya University Press: Nagoya, Japan, 1997 (in Japanese).

(4) Dagani, R. *Chem. Eng. News* **1999**, *77*, 54−59.

(5) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Chem. Phys.* **1993**, *97*, 3379−3383.

(6) Ruoff, R. S.; Malhotra, R.; Huestis, D. L.; Tse, D. S.; Lorents, D. C. *Nature* **1993**, *362*, 140−141.

(7) Doome, R. J.; Fonseca, A.; Nagy, J. B. *Colloids and Surf. A* **1999**, *158*, 137−143.

(8) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506−6509.

(9) Sano, M.; Oishi, K.; Ishi-i, T.; Shinkai, S. *Langmuir* **2000**, *16*, 3773−3776.

(10) Sijbesma, R.; Srdanov, G.; Wudl, F.; Castoro, J. A.; Wilkins, C.; Friedman, S. H.; DeCamp, D. L.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6510−6512.

(11) Dugan, L. L.; Turetsky, D. M.; Du, C.; Lobner, D.; Wheeler, M.; Almli, C. R.; Shen, C. K.-F.; Luh, T.-Y.; Choi, D. W.; Lin, T.-S. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 9434−9439.

(12) Brettreich, M.; Hirsch, A. *Tetrahedron Lett.* **1998**, *39*, 2731−2734.

(13) Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604−606.

(14) Lai, D. T.; Neumann, M. A.; Matsumoto, M.; Sunamoto, J. *Chem. Lett.* **2000**, 64−65.

(15) Scrivens, W. A.; Tour, J. M.; Creek, K. E.; Pirisi, L. *J. Am. Chem. Soc.* **1994**, *116*, 4517−4518.

(16) Takahashi, H.; Ozaki, M. *Studies in Surface Science and Catalysis*; Iwasawa, Y., Oyama, N., Kunieda, H., Eds.; Elsevier Science: Tokyo, 2001; Vol. 132, pp 419−422.

(17) Andrievsky, G. V.; Kosevich, M. V.; Vovk, O. M.; Shelkovsky, V. S.; Vaschenko, L. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1281−1282.

(18) Mchedlov-Petrossyan, N. O.; Klochkov, V. K.; Andrievsky, G. V. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 4343−4346.

(19) Wang, X.; Goh, S. H.; Lu, Z. H.; Lee, S. Y.; Wu, C. *Macromolecules* **1999**, *32*, 2786−2788.

(20) Tang, B. Z.; Peng, H.; Leung, S. M.; Au, C. F.; Poon, W. H.; Chen, H.; Wu, X.; Fok, M. W.; Yu, N.-T.; Hiraoka, H.; Song, C.; Fu, J.; Ge, W.; Wong, G. K. L.; Monde, T.; Nemoto, F.; Su, K. C. *Macromolecules* **1998**, *31*, 103−108.

(21) Tang, B. Z.; Xu, H.; Lam, J. W. Y.; Lee, P. P. S.; Xu, K.; Sun, Q.; Cheuk, K. K. L. *Chem. Mater.* **2000**, *12*, 1446−1455.

(22) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903−1907.

(23) Chen, X. L.; Jenekhe, S. A. *Langmuir* **1999**, *15*, 8007−8017.

10.1021/ja010202a CCC: \$20.00

fractions of the polar solvent in binary solvent mixtures was found to be due to the aggregation of fullerene molecules.[24-27] Aggregation of C_{60} in neat solvents has been also reported.[27,28] It has been found that the photophysical and photochemical properties of aggregated fullerene molecules are significantly different than those of free C_{60} or C_{70} molecules in the solution.[24-30] The aggregation behavior of the fullerene molecules presents another interesting phenomenon added to the unique properties of buckyballs and deserves study in detail.

The work reported in this paper is aimed at studying the formation and stability of colloidal dispersions of C_{60}, C_{70}, and their mixture in polar organic solvents that are found to be nonsolvents or poor solvents for these molecules. The spontaneous formation of stable particles with size in the colloidal range and relatively low polydispersity was found when a true solution of fullerene was added in small portions into a polar liquid. Various solvent combinations and the influence of preparation procedure, fullerene type, and concentration were examined. Colloidal dispersions of C_{60}/C_{70} mixtures were also prepared and the particle size was found to exhibit interesting behavior as a function of fullerene ratio. The main factors governing the size of the fullerene particles and the possible mechanism of formation are explored and discussed.

Experimental Section

Materials. Three fullerene samples have been used in this study: Fullerene extract (C_{60} containing 20% C_{70} and small amounts of higher fullerenes) referred as C_{mix} in the text below, C_{60} (>99.9%), and C_{70} (>98%). All were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and used as received. The analytical-grade solvents [toluene, xylene, benzene, 1-methylnaphthalene, *N*-methyl-2-pyrrolidinone (NMP), acetonitrile, acetone, ethanol, hexane, chloroform, tetrahydrofuran (THF), and dioxane] manufactured by Wako Pure Chemicals Industries Ltd. (Osaka, Japan), were used without further purification.

Preparation of Dispersions. The preparation of the colloidal dispersions of fullerenes in polar organic solvents was easy and rapid. First, true solutions of C_{60}, C_{mix}, and C_{70} were prepared with organic solvents that are known to dissolve them in the molecular state (for instance, toluene, 1-methylnaphthalene, and NMP). The solutions were stirred at least for 2 days in a dark place, and then filtered through 0.2 μm hydrophobic PTFE filters (Nihon Millipore Ltd., Japan) in order to remove dust and remaining solid fullerenes; the total concentration of fullerene was determined by UV spectroscopy. Next, a given small volume (5−50 μL) of the toluene solution was added into the larger volume (5−20 mL) of a polar solvent (acetonitrile, ethanol, or acetone) and the sample was shaken by hand for homogenization. Immediately after mixing of the solutions, the color of the sample changed and the simultaneous formation of particles with size in the colloidal range was detected by dynamic light scattering (DLS) measurements. The violet color of C_{60} turned into orange-brown, while the color of C_{70} changed from red-brown into brown-violet after their toluene solutions were mixed with acetonitrile. In fact, this experimental procedure resembles the reprecipitation method.[31] A similar procedure for preparingorganic microcrystals by dispersing ethanol or acetone solutions of compounds into stirred water also has been described in the literature.[32-35] In our experiments we found that the stirring of the nonsolvent during the process of mixing was not necessary because it does not influence the size distribution of the formed particles and no additional treatment was needed to stop the process of particle growth or to initiate a crystallization. In fact, in our case the process of particle formation was fast and the equilibrium average size of the fullerene dispersion was established almost immediately after the reprecipitation in most of the cases studied, unlike the situation of growing organic microcrystals.[33-35] We found also that when the toluene solution with a given concentration of C_{60} was added gradually *in small portions* into the polar organic solvent (acetonitrile), concentrated dispersions of fullerenes were prepared without significant change in the particle size. However, addition of the nonsolvent in the same way into the true fullerene solution, or quick mixing of comparable amounts of fullerene solution and the nonsolvent, led to the formation of larger particles with broader size distribution.

It turned out that a necessary condition for the spontaneous formation of colloid particles is the dissolution of fullerene into a good solvent prior to mixing with acetonitrile. Our attempts to redisperse the dried fullerene content once previously dispersed into acetonitrile were unsuccessful even when acetonitrile was mixed with toluene in advance. However, in all cases the solute dried in nitrogen or air atmosphere was redissolved easily in toluene, showing the same characteristic UV−VIS spectra as the fresh toluene solutions of C_{60}, C_{70}, and C_{mix}. The presence of additional peaks that would suggest the formation of fullerene derivatives was not observed even after long storage of colloidal dispersions.

Experimental Methods. The formation and the stability of the colloidal dispersions of fullerenes in the polar organic solvents were studied mainly with DLS. The diffusion coefficient of the particles, D, was measured on a DLS-820 light scattering system (Otsuka Electronics Co., Ltd., Osaka, Japan) equipped with He−Ne laser (10 mW) operating at 632.8 nm wavelength. The system allows DLS measurements at various scattering angles between 20° and 150°. Since our preliminary experiments showed no angular dependence of the particle size, most DLS measurements were performed at 90°. The autocorrelation function of the intensity was analyzed by cumulant[36] analysis to obtain the average diffusion coefficient, D, of the fullerene particles and polydispersity index. The hydrodynamic diameter, d_h, was calculated by means of the Stokes−Einstein equation[36] ($d_h = k_BT/3\pi\eta D$, where k_BT is the thermal energy and η is the viscosity of the continuous phase). In the cumulant method the natural logarithm of the autocorrelation function $g^{(1)}(\tau)$ versus τ is fitted to the second-order polynomial. The coefficient of the first-order term (first cumulant) is an average decay rate, Dq^2 [$q = (4\pi n/\lambda) \sin(\theta/2)$, where n is the refractive index, λ is the wavelength of the incident light, and θ is the scattering angle], while the second cumulant is related to the polydispersity of the sample. The autocorrelation function was also analyzed by the Marquardt[37] (histogram) method to obtain the size distribution functions.

Electron microscopic pictures showed that the particles are roughly spherical. They have many edges and rough surfaces but their size is close to the average size determined by DLS experiments. Hence, the hydrodynamic diameter, d_h, can be used to study the formation and the behavior of the fullerene dispersions at various experimental conditions. All samples were slightly colored, and in order to avoid the influence of light absorbance we kept the particle concentration low. The absorbance of dispersions measured at 632.8 nm was between 0.01 and 0.22 depending on the fullerene type and concentration. The

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(24) Sun, Y.-P.; Bunker, C. E. *Nature* **1993**, *365*, 398.

(25) Ghosh, H. N.; Sapre, A. V.; Mittal, J. P. *J. Phys. Chem.* **1996**, *100*, 9439−9443.

(26) Mrzel, A.; Mertelj, A.; Omerzu, A.; Copic, M.; Mihailovic, D. *J. Phys. Chem. B* **1999**, *103*, 11256−11260.

(27) Rudalevige, T.; Francis, A. H.; Zand, R. *J. Phys. Chem. A* **1998**, *102*, 9797−9802.

(28) Nath, S.; Pal, H.; Palit, D. K.; Sapre, A. V.; Mittal, J. P. *J. Phys. Chem. B* **1998**, *102*, 10158−10164.

(29) Fujitsuka, M.; Kasai, H.; Masuhara, A.; Okada, S.; Oikawa, H.; Nakanishi, H.; Watanabe, A.; Ito, O. *Chem. Lett.* **1997**, 1211−1212.

(30) Fujitsuka, M.; Kasai, H.; Masahara, A.; Okada, S.; Oikawa, H.; Nakanishi, H.; Ito, O.; Yase, K. *J. Photochem. Photobiol. A: Chem.* **2000**, *133*, 45−50.

(31) Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford, U.K., 1995; Vol. 1.

(32) Kasai, H.; Nalwa, H. S.; Oikawa, H.; Okada, S.; Matsuda, H.; Minami, N.; Kakuta, A.; Ono, K.; Mukoh, A.; Nakanishi, H. *Jpn. J. Appl. Phys.* **1992**, *31*, L1132−L1134.

(33) Kasai, H.; Oikawa, H.; Okada, S.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2597−2601.

(34) Nakanishi, H.; Katagi, H. *Supramol. Sci.* **1998**, *5*, 289−295.

(35) Oikawa, H.; Oshikiri, T.; Kasai, H.; Okada, S.; Tripathy, S. K.; Nakanishi, H. *Polym. Adv. Technol.* **2000**, *11*, 783−790.

(36) Schmitz, K. S. *An Introduction to Dynamic Light Scattering by Macromolecules*; Academic Press: San Diego, CA, 1990.

(37) Marquardt, D. M. *J. Soc. Industr. Appl. Math.* **1963**, *11*, 431−441.

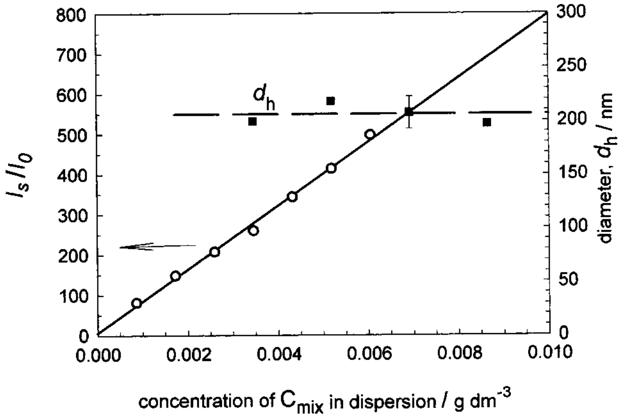

Figure 1. Intensity of light scattered by the colloidal dispersions of C_{mix} in toluene/acetonitrile, I_s, normalized by its value measured for pure acetonitrile, I_0, and the average hydrodynamic diameter of the particles, d_h, as a function of fullerene concentration in the dispersion.

experiments carried out at different intensities of the laser beam showed that the measured diffusion coefficient does not depend on the power of incident light and suggested that the influence of light absorbance is negligible.[36,38]

DLS measurements showed that the size of the fullerene particles is determined immediately after mixing of the fullerene solution with the polar medium and almost does not change with time. Only in the case of pure C_{60} a slight growth (up to 10−15%) of the particle diameter was observed during the first hour after the preparation at some concentrations. All results reported in this paper were measured at least 1 h after preparation.

The colloidal dispersions of fullerenes were also studied by high-resolution transmission electron microscopy (HRTEM). The HRTEM experiments, done to check the particles structure, were carried out by Nissan Arc Co. Ltd. (Yokosuka, Japan).

Electrophoretic light scattering (ELS) experiments were performed at the facilities of Otsuka Electronics Co., Ltd., (Tokyo, Japan). They were done to study the charge of the fullerene colloidal particles.

The UV−VIS spectra were recorded on a Shimadzu UV-2400PC spectrophotometer (Shimadzu, Kyoto, Japan) using a quartz cuvette with 1 cm optical path. UV−VIS spectroscopy was used to study the concentration and the chemical stability of fullerenes. The latter was checked by high-performance liquid chromatography (HPLC) as well.

Results

Formation of Fullerene Particles. The mixing of solution of C_{mix} in toluene with acetonitrile resulted in the formation of a sample with different color and exhibiting slight opalescence. Figure 1 shows the normalized intensity of the light scattered by the sample, I_s/I_0, as a function of C_{mix} concentration in the acetonitrile solution. The fullerene concentration in this case is varied by increasing the amount of toluene solution containing 1.7 g/dm^3 C_{mix} added to a constant volume of acetonitrile. One sees that I_s/I_0 increases linearly with fullerene concentration. Since the intensity of the scattered light is a linear function of the particle number concentration and depends much more strongly on their size,[36] the increase in C_{mix} concentration in this case leads to an increase in the number of particles only. Thus the formation of fullerene colloidal dispersions is very fast and takes place immediately after the first drops of toluene solution of fullerene are added into the acetonitrile. The next portions of the toluene solution result in the formation of new particles and do not increase the size of already existing ones.

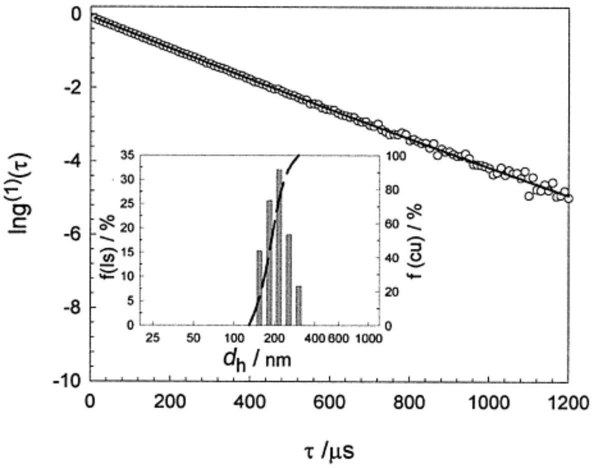

Figure 2. Logarithm of the autocorrelation function, $g^{(1)}(\tau)$, versus time, τ, for a colloidal dispersion of C_{mix} in toluene/acetonitrile. (○) Experimental data; (—) fit according to the second-order cumulant analysis. The inset shows the size distribution functions of the same sample: distribution mean diameter is 212 nm.

This observation is confirmed by the size measurements. The results for the size of the fullerene particles, presented in Figure 1 (■), show that the average hydrodynamic diameter, d_h, is about 210 nm (---) and remains constant in the concentration range studied within experimental error. It should be noted that every point in Figure 1 corresponds to a separately prepared sample, and hence the scattering of the data around the dashed line reflects also the experimental error due to the preparation procedure.

The polydispersity of the fullerene colloid particles is fairly low. This is clearly seen in Figure 2, where the logarithm of the normalized autocorrelation function is shown as well as the intensity size distribution (inset in Figure 2) obtained for one of the studied samples. The solid line presents the fit of the experimentally measured autocorrelation function with the second-order polynomial equation according to the cumulant analysis. Its linearity indicates the low polydispersity of the sample. Indeed the calculated polydispersity index in all cases was below 0.1. In addition, the size distribution, shown in the inset of Figure 2 and calculated independently by Marquardt analysis, is relatively narrow and also suggests low polydispersity of the fullerene dispersion.

We studied the behavior of fullerene particles formed in acetonitrile upon dilution with the dispersion medium. Figure 3 shows that the particle size does not change noticeably with C_{mix} concentration and consequently the fullerene particles do not dissolve upon dilution with the polar solvent. This result is not surprising because the fullerenes studied are not soluble in acetonitrile. Both dependencies in Figure 3 show a slight increase in the hydrodynamic diameter when C_{mix} concentration is reduced. We may speculate that this effect reflects the influence of the repulsive interactions on the diffusion coefficient measured by DLS.[36,39] As will be seen later, the repulsive interactions between fullerene particles are quite possible. However, the detected change is close to the experimental error and it is difficult to extract information about interparticle interactions.

Colloidal Dispersions of Fullerenes in Various Solvent Combinations. Figure 3 shows that the average size of the dispersions prepared from true solutions of C_{mix} in toluene and 1-methylnaphthalene is similar. To investigate in greater detail

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(38) Hall, R. S.; Oh, Y. S.; Johnston, C. S. *J. Phys. Chem.* **1980**, *84*, 756−767.

(39) Pecora, R. *Dynamic Light Scattering*; Plenum Press: London, 1985.

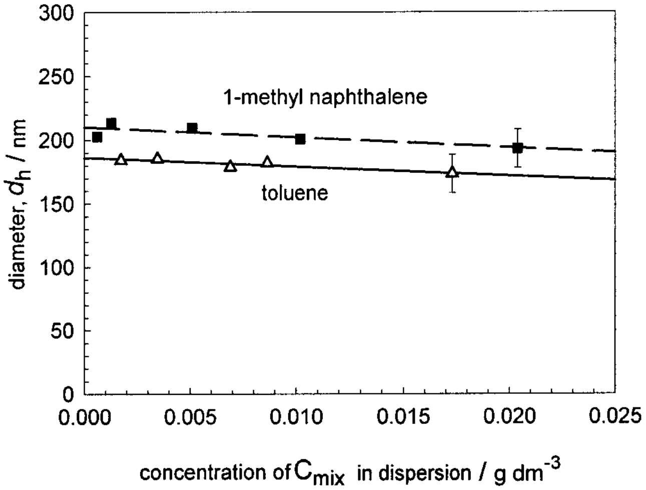

Figure 3. Concentration dependence of the hydrodynamic diameter, d_h, of colloidal dispersions of C_{mix} in acetonitrile. The fullerene concentration is decreased by diluting the most concentrated samples (the right points) with acetonitrile. C_{mix} is initially dissolved in toluene (△) and in 1-methylnaphthalene (■).

Table 1. Average Hydrodynamic Diameter, d_h, of Fullerene Particles Formed When True Solutions of C_{mix} in Various Solvents Are Mixed with Acetonitrile

solvent	d_h (nm)	dielectric constant[b] ϵ	solubility of C_{60} (g/dm^3)
benzene	207 ± 30	2.3 (293.2 K)	1.7[c]
toluene	210 ± 30	2.4 (296.4 K)	2.8[c]
xylene	240 ± 35	2.4 (293.2 K)	5.2[c]
1-methylnaphthalene	229 ± 30	2.9 (293.2 K)	33.0[c]
chloroform	210 ± 25	4.8 (293.2 K)	0.16[c]
THF	226 ± 20	7.5 (295.2 K)	0.009[d]
NMP	150 ± 20	32.2 (298.2 K)	0.89[c]

[a] The concentration of C_{mix} in the aromatic solvents is 1.7 g/dm^3. In all other cases saturated solutions of C_{mix} are used. Dielectric constants of the solvents and the solubility of C_{60} are also listed. [b] Reference 47. [c] Reference 5. [d] Reference 40.

the influence of the type of solvent on the formation and the average size of the fullerene dispersions, we used some organic solvents known to dissolve fullerene molecules to a different extent.[3,5] Table 1 shows that the particle size varies slightly from solvent to solvent but remains in the 150−250 nm range. The variations in the particle size could be related to the different C_{mix} concentrations in the nonaromatic solvents. As shown below, reduction of the fullerene concentration in toluene decreases the size of particles in acetonitrile. In the case of aromatic solvents, the size is smallest for benzene and the largest in the presence of xylene, but the differences are not much bigger than experimental error. It is known from the literature that the solubility of C_{60} increases with the size of the aromatic molecule from benzene to 1-methylnaphthalene[5] (see Table 1). However, it seems that this effect does not influence significantly the size of the colloid particles formed in acetonitrile. The solubility of C_{60} in 1-methylnaphthalene is 1 order of magnitude higher than in benzene, toluene, and xylene,[5] but the size of the particles is almost the same in all cases. It is seen also that the polarity (dielectric constant) of the solvents does not have a significant effect on the particle size. For instance, NMP is a polar solvent (it has a dielectric constant of 32.2) but it exhibits good solubility of C_{60} (comparable to that in toluene), being an exception among the good solvents for fullerenes. Our experiments with NMP/acetonitrile samples show that the formation of colloid fullerene particles is similar to the process in aromatic solvents. The average diameter of the particles is about 150 nm and it does not differ markedly from the size measured in aromatic solvents with the same fullerene concentration. One can draw the conclusion that interactions between the molecules of the good solvent and the fullerene are not of primary importance in determining the size of the particles.

Table 2. Average Hydrodynamic Diameter, d_h, of Fullerene Particles Formed When Toluene Containing 0.9 g/dm^3 Fullerene Is Added to Different Nonsolvents[a]

	d_h (nm)			dielectric constant[b]
polar solvent	C_{mix}	C_{60}	C_{70}	ϵ (293.2 K)
acetonitrile	194	392	285	36.6
ethanol	280	490	358.5	25.3
acetone	225			21.0

[a] The concentration of fullerene in the colloidal dispersions is 0.01 g/dm^3. [b] Reference 47.

Table 2 lists the results for the size of the particles when toluene solutions of fullerenes were mixed with different organic solvents whose dielectric constant is larger than 20. It is seen that colloidal dispersions are formed in all of the solvents studied. For a given fullerene the diameter of the colloid particles varies with the type of the nonsolvent but in all cases it is below 0.5 μm. Colloidal dispersions in ethanol have larger average size. We tried to prepare samples using solvents with lower dielectric constant as poor solvents for C_{60}, but the formation of colloidal particles in hexane, chloroform, and dioxane was not observed. It is worth mentioning that it is possible to prepare colloidal dispersions in water by the same procedure, as described in the Experimental Section. For this purpose a good solvent for fullerene that is miscible with water is needed. For instance, the combination of C_{mix} solution in NMP and water works well, and colloidal dispersions with average size around 80−90 nm and relatively low polydispersity are obtained. The size of the particles is about half that of the acetonitrile sample prepared under exactly the same conditions. The samples show the same colloid stability as those prepared in toluene/acetonitrile systems. The formation of fullerene dispersions in water is described elsewhere[40] and no further details are given here. One may speculate that the increasing polarity of the dispersion medium leads to the formation of smaller particles (see also Table 2), although acetone is an exception. The importance of the dielectric constant of the poor solvent for the solvatochromism exhibited by C_{60} in binary solvent mixtures was also revealed in a qualitative study when its pyridine solution was diluted with various nonsolvents.[26]

Influence of the Fullerene Type on the Particle Size. Table 2 shows an interesting phenomenon: under the same conditions, the size of particles formed by different fullerenes in a given nonsolvent is different. The largest are the particles formed by C_{60} molecules, while C_{mix} particles are smaller than the average size of colloidal dispersions of both pure substances. The size distributions of the samples prepared from toluene/acetonitrile combination are shown in Figure 4. The difference in the size of the particles formed by pure C_{60} and C_{70} under the same conditions could be related to the slightly different size[1] and the symmetry of the fullerene molecules[1] that may affect packing. The influence of C_{70} molecules on the particle size in mixed samples is more clearly seen in Figure 5. It presents the diameter of particles formed in acetonitrile when the added toluene solution contains mixture of pure C_{60} and C_{70} as a function of the weight fraction of C_{70} in the fullerene mixture. The total fullerene concentration in toluene is kept constant and

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(40) Deguchi, S.; Alargova, R. G.; Tsujii, K. *Langmuir* **2001**, *17*, 6013−6017.

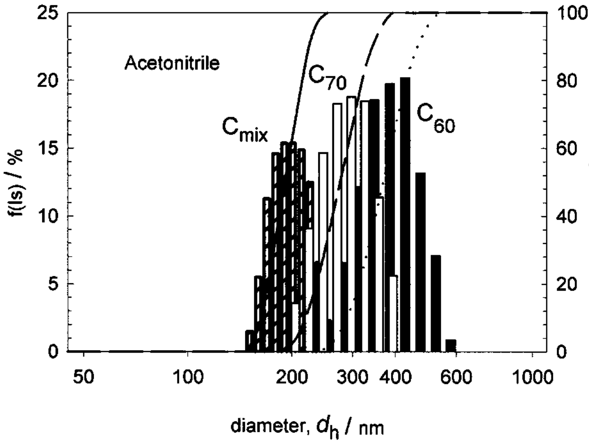

Figure 4. Size distribution functions of the colloidal dispersions formed by C_{60}, C_{70}, and C_{mix} in acetonitrile. Fullerenes were initially dissolved in toluene. The concentration of fullerene in the dispersions is 0.01 g/dm^3.

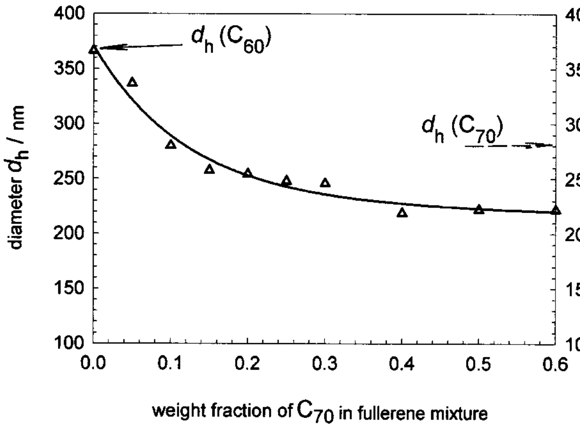

Figure 5. Hydrodynamic diameter, d_h, of fullerene dispersions in toluene/acetonitrile presented as a function of the weight fraction of C_{70} in fullerene mixture. The total concentration of fullerene in toluene is kept constant at 0.9 g/dm^3. The ratio between C_{60} and C_{70} is varied in the toluene solution. The volumes of toluene and acetonitrile are kept constant. The dashed arrow indicates the average size of C_{70} measured under the same conditions.

only the weight ratio between the two fullerenes is changed. The left point corresponds to the result measured for pure C_{60}. The size of pure C_{70} particles, prepared under the same conditions, is indicated by the dashed arrow in Figure 5. It is seen that replacing C_{60} molecules by C_{70} ones reduces the particle size even at 0.05 weight fraction of C_{70}. This decrease is more pronounced at low weight fractions of C_{70}. The curve levels off at about 0.4 weight fraction. In the region corresponding to more than 0.1 weight fraction of C_{70}, the size of the mixed particles is smaller than that corresponding to each pure fullerene. The effect appears to be due to the possibility for closer packing of molecules with different sizes. Note that the size of particles formed at 0.2 weight fraction of C_{70} is larger than the size measured for C_{mix} in toluene/acetonitrile. This difference is probably related to the purity and slightly different composition of the solid fullerene samples.

Structure of Fullerene Particles. The structure of the fullerene particles was studied by HRTEM. Figure 6 presents two electron micrographs of a colloid particle formed in toluene/acetonitrile sample containing mixture of C_{60} and C_{70}. The pictures show regular ordering of the fullerene molecules. There are some disordered domains that are more clearly seen in Figure 6b. The average center-to-center distance between the fullerene molecules is roughly estimated from these pictures to be about 1.0 nm. This value is in agreement with those determined for the crystal lattice of solid C_{60} and C_{70}.[1] Therefore, the fullerene colloid particles are formed as a result of crystallization process.

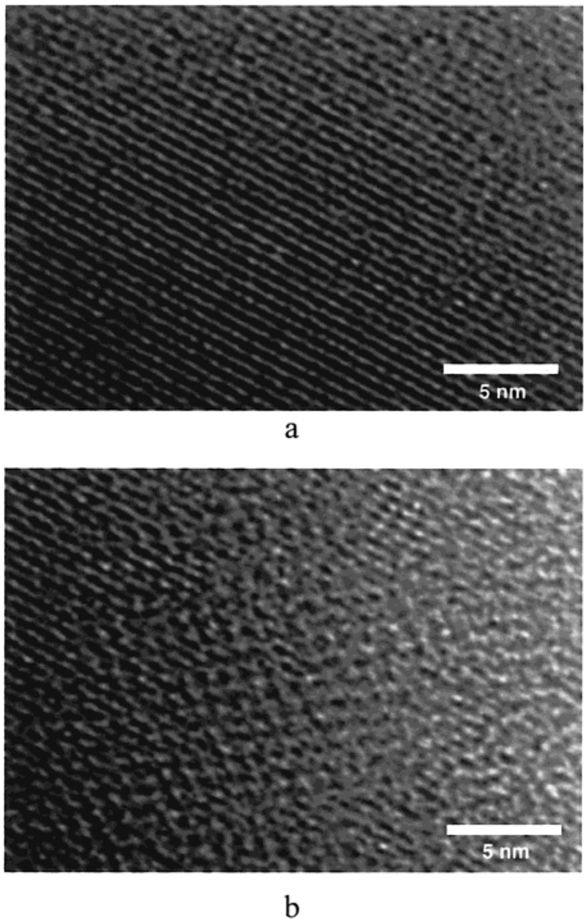

Figure 6. HRTEM pictures of a fullerene particle formed in toluene/acetonitrile. Panels a and b show different portions of the same particle. The toluene solution contained a mixture of 50% C_{60} and 50% C_{70}. The total fullerene concentration in the dispersion is 0.01 g/dm^3.

Long-Term Stability. Some colloidal dispersions of C_{mix} in toluene/acetonitrile were stored for about one year in a dark place and the size of the particles was measured as a function of time. Figure 7 (top) presents the average hydrodynamic diameter of the fullerene particles plotted vs C_{mix} concentration in the dispersion. DLS measurements were performed 1 day, 5 days, 3 months, and 10 months after the preparation of the samples. The results measured for a given sample show no significant change and no systematic deviation in the average size with time. The size distributions for one of the samples measured with DLS 1 day and 10 months after the preparation are given in Figure 7 (bottom). The broadness of distribution is the same in both cases. A colloidal dispersion of C_{mix} in toluene/acetonitrile was separated into two parts and one of them was exposed to daylight for 1 month, while the other was kept in the dark. DLS measurements show no significant difference in the particle size distribution during that period.

The samples prepared in acetonitrile and ethanol showed sedimentation over time due to the density difference between the dispersion medium and the fullerene particles. However, they completely reverted to homogeneous dispersions after shaking. The samples prepared from NMP/water did not give

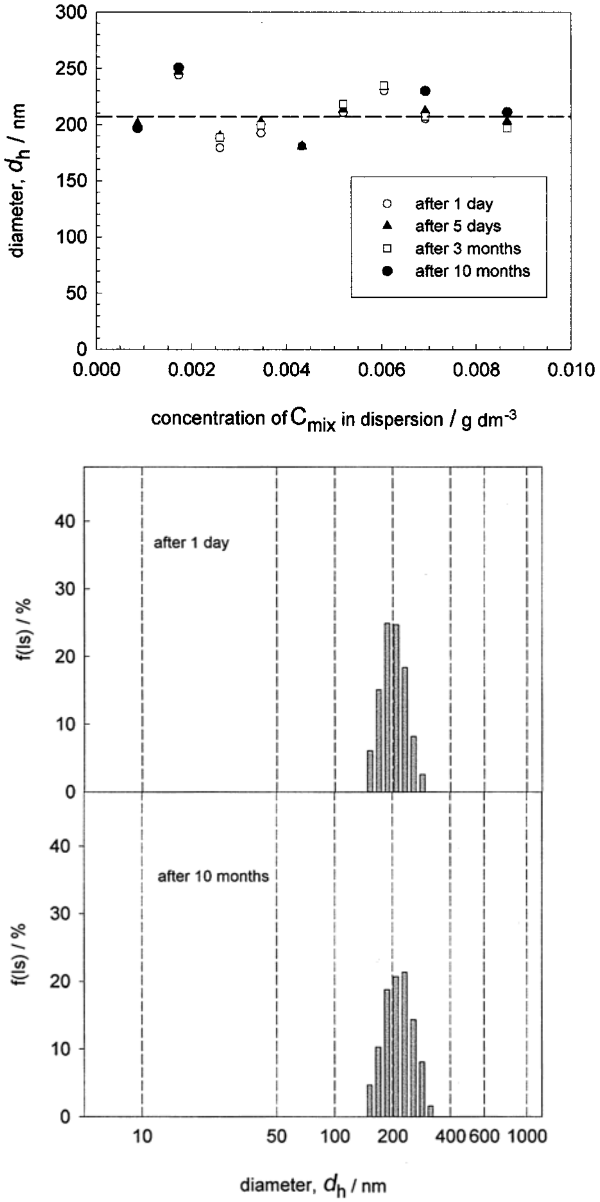

Figure 7. (a, top panel) Effect of storage time on the average hydrodynamic diameter, d_h, of fullerene dispersions in toluene/acetonitrile presented as a function of C_{mix} concentration in the dispersion. The concentration of fullerene in toluene is 1.7 g/dm^3. The fullerene concentration in the dispersion is increased with increasing the volume of toluene solution added to acetonitrile. (b, bottom panel) Size distributions of a colloidal dispersion formed by C_{mix} in acetonitrile, measured 1 day or 10 months after preparation.

sediment due to the higher density of water and smaller size of the colloid particles.

To understand the reasons for the colloid stability of the fullerene dispersions, ELS measurements with some of the samples were carried out. The results for the electrophoretic mobility of the fullerene particles formed in toluene/acetonitrile samples containing pure and mixed C_{60} and C_{70} are summarized in Table 3. It is seen that the particles are negatively charged and the magnitude of electrophoretic mobility turns out to be relatively insensitive to the content of C_{60} or C_{70}. ζ-potentials calculated from the Smoluchovsky equation[31] are also given in Table 3. They are similar to the values obtained for the fullerene colloidal particles formed in water.[40]

Table 3. Electrophoretic Mobility and ζ-potential Obtained for Colloidal Dispersions of C_{60}, C_{70}, and Their Mixtures in Acetonitrile[a]

sample	$10^4 \times$ electrophoretic mobility (cm^2/V·s)	ζ-potential (mV)
C_{60}	−3.30	−32.5
80 wt % C_{60}/ 20 wt % C_{70}	−3.80	−38.5
50 wt % C_{60}/ 50 wt % C_{70}	−3.65	−36.3
C_{70}	−3.40	−34.2

[a] Fullerenes were initially dissolved in toluene. The total concentration of fullerene in the colloidal dispersions is 0.01 g/dm^3.

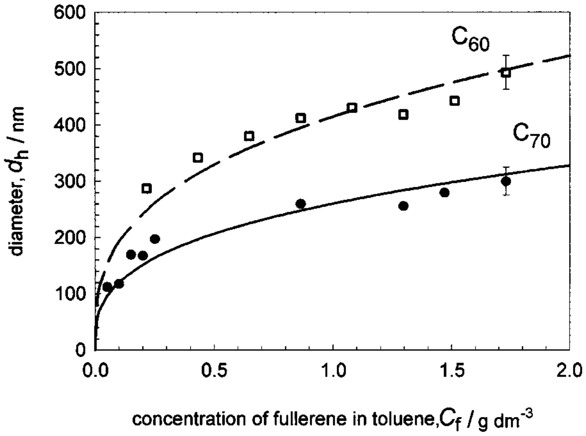

Figure 8. Hydrodynamic diameter of fullerene particles formed in acetonitrile as a function of the fullerene concentration in the toluene solution, C_f. (□) Results measured for C_{60}; (●) results measured for C_{70}. The lines are drawn according to the prediction of the model described in the Discussion Section.

Influence of Fullerene Concentration in the Initial Solution. Colloidal dispersions of fullerenes in acetonitrile were prepared from toluene solutions with various concentrations of C_{60} and C_{70}. In both cases an increase in the particle size with increasing concentration of fullerene in the toluene solution was observed. Figure 8 shows the diameter of C_{60} and C_{70} particles as a function of fullerene concentration in the toluene solution, C_f. All samples were prepared at constant volume ratio between toluene solution and acetonitrile. The concentration of fullerene in the dispersion is 200 times smaller than in toluene. The size of the C_{70} colloidal particles increases roughly 2-fold in the concentration range studied. At the lowest fullerene concentrations, the intensity of the scattered light was low and the accuracy of the data was not very good. It was not possible to carry out DLS measurements to check if particles with size smaller than 100 nm exist or not.

Discussion

Possible Mechanism of Formation of Fullerene Dispersions. With the experimental observations mentioned in the previous section in mind (namely, the spontaneous formation of colloid particles with definite size and crystalline structure), we may consider the following simple model, which describes the mechanism of dispersion formation (see Figure 9): instantaneous small emulsion droplets of toluene are formed immediately after mixing with acetonitrile. They exist for a very short period of time, because toluene is completely miscible with acetonitrile and its molecules begin to diffuse in the dispersion medium. The contact of fullerene molecules with the polar medium is energetically unfavorable and they prefer to stay surrounded by toluene molecules. When the concentration of fullerene inside the toluene droplets reaches the saturation

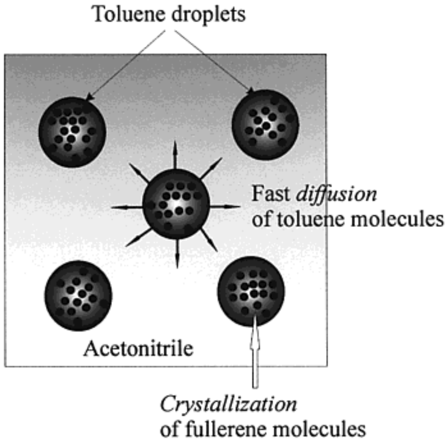

Figure 9. Schematic representation of the mechanism suggested for the formation of fullerene dispersions.

point, the crystallization process quickly takes place and fullerene microcrystals are formed. Initial formation of fine droplets of the precipitated solution has been also suggested as a first stage in the formation of organic microcrystals.[33−35] However, in their case depending on the nature of the organic compound these droplets lead to formation of small clusters producing the nuclei for the crystallization process[33] that grow to microcrystals or to formation of amorphous particles that further bind together or with small microcrystals to give larger particles in which crystallization of organic molecules occurs.[34,35] Our model suggests that each emulsion droplet leads to the formation of one colloidal particle. If we assume that the size of the toluene droplets is uniform and independent of the fullerene concentration, and that the droplets do not coalesce during their short existence, the model gives the following simple relation between the diameter of colloid particles, d_h, and the weight concentration of fullerene in the initial solution, C_f:

$$d_h = 2R\left(\frac{v_f N_A}{\phi M}\right)^{1/3} C_f^{\,1/3} \qquad (1)$$

where R is the radius of the droplets formed by the good solvent, v_f and M are the molecular volume and the molar mass of the fullerene, and ϕ is the volume fraction of fullerene molecules in a colloid particle. According to eq 1, the size of the particles formed by the molecules of a given fullerene will increase with its concentration in the toluene solution, and this is what is seen in Figure 8. The model suggests also that the size of the fullerene particles will remain the same, independent of the volume of the added true solution when the fullerene concentration in the latter is kept constant, and hence it is in qualitative agreement with the data shown in Figures 1 and 7a.

Under the same conditions, the size of particles will be larger for a fullerene with smaller molar mass, M, or larger molecular volume, v_f. Figure 10 presents the predictions of the model for the size of particles formed by C_{60} and C_{70} molecules with the assumption that $R = 2.5$ μm and $\phi = 0.74$ (close packing of molecules) in both cases. At a given concentration the diameter of particles will depend on the properties of the fullerene, the packing of molecules in the particles, ϕ, and the size of the droplets, R. The predicted size for C_{60} is larger than C_{70} because the latter is more compact ($v_f = 1.87 \times 10^{-22}$ cm^3 for C_{60} and $v_f = 1.56 \times 10^{-22}$ cm^3 for C_{70} molecule[1]). The increase in particle diameter is steeper at lower concentrations, and particles smaller than 100 nm in diameter should be formed at very low concentrations of the true solution. This behavior is also seen in Figure 8, presenting the experimental data where the lines are drawn according to eq 1 with one adjustable parameter—the size of toluene droplets. Close packing is assumed in both cases and calculations were performed with $\phi = 0.74$. R is determined to be 2.4 μm in the case of C_{70} and 3.5 μm for C_{60}. Of course it is possible that the packing of C_{60} and C_{70} molecules is different and different values of ϕ should be used for each fullerene. The size of emulsion droplets formed by the good solvent most probably depends on the properties of both solvents, and this could be one of the reasons for the small differences observed for a given fullerene with different solvent combinations. The proposed model is too simple to describe quantitatively all aspects of the formation of fullerene colloidal dispersions, but it explains in a reasonable way the main observations for particle size as a function of fullerene concentration. Note again that the formation and size of particles depend on the preparation procedure. The mechanism of formation and the structure of particles when solutions of fullerenes in good solvents are diluted with polar liquid could be different. In the case of toluene/acetonitrile combination, the formation of larger fullerene particles with broader size distribution was observed, similar to the results reported in the literature for the concentration range studied.[25,27] It was shown that in this case fullerene aggregates with fractal structure are formed.[27]

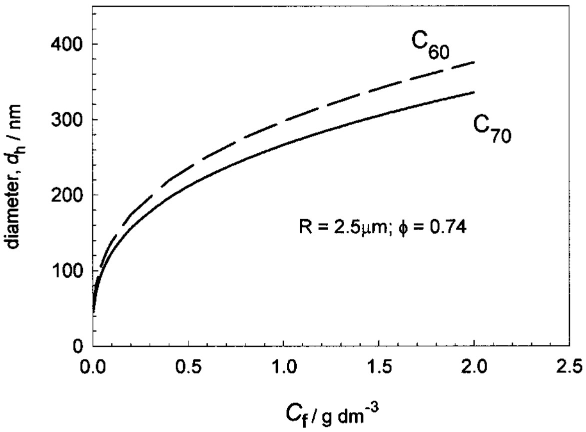

Figure 10. Diameter of C_{60} (---) and C_{70} (—) particles, calculated from eq 1, as a function of the fullerene concentration in toluene solution, C_f. In both cases the radius of the drops was chosen to be $R = 2.5$ μm, and the close packing of fullerene molecules is assumed, i.e., $\phi = 0.74$.

One should note that the group of Nakanishi et al.[29,30] has applied the reprecipitation method to fabricate C_{60} microcrystals with size in the colloidal range using a carbon disulfide/ethanol combination. However, they concluded later[41] that the usual reprecipitation method is not applicable to preparing C_{60} microcrystals from other solvent combinations owing to the low solubility of this fullerene, and they have used a high-temperature and high-pressure liquid crystallization method to prepare C_{60} microcrystals.[41] In our study we show that it is possible to use other solvent combinations to prepare fullerene colloid particles when polar organic solvents are chosen for a dispersion medium.

Colloid Stability of Fullerene Dispersions. The stability of fullerene dispersions after formation is determined by the interparticle interactions. The magnitude of the calculated ζ-potential (see Table 3) suggests that electrostatic repulsive interactions play an important role for colloid stability of fullerene dispersions. Although the origin of the surface charge

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[41] Kasai, H.; Okazaki, S.; Hanada, T.; Okada, S.; Oikawa, H.; Adschiri, T.; Arai, K.; Yase, K.; Nakanishi, H. *Chem. Lett.* **2000**, 1392−1393.

is not known, one may conclude that the charging of the particles is related to the properties of the nonsolvent, since stable fullerene dispersions are not formed, for instance, in hexane. In fact, the formation of stable colloidal dispersions of fullerenes is observed in solvents with dielectric constants higher than 20. All of them contain atoms possessing lone pairs of electrons and may act as electron donors. The negative surface potential may originate from electron transfer in solvent/solute interactions. It is known that each molecule of C_{60} and C_{70} is able to accept up to six electrons and their anions are detected under some special conditions.[1,42−44] The absorption of some negative ions or directional ordering of the polar solvent molecules in the vicinity of the particle surface could also lead to a potential difference between the bulk dispersion medium and the interface. Fullerene microcrystals may also include molecules of the good solvent. The formation of solvated crystals of C_{60} in toluene, benzene, and hexane under particular conditions has been reported in the literature.[1,45,46]

Conclusions

It is shown that C_{60} and C_{70} fullerenes can be dispersed in polar organic solvents that are nonsolvents or poor solvents for these molecules, due to the formation of colloids. The fullerene particles have a relatively narrow size distribution and are prepared simply by mixing a solution of fullerene (C_{60}, C_{70}, or a mixture) in a good solvent with a polar organic solvent. The most interesting observations are the spontaneous formation of the fullerene particles with average size in the colloidal range, relatively narrow size distribution, and good colloid stability of the samples. The colloidal dispersions remain stable for more than 10 months without any stabilizers. Electrophoretic mobility measurements show that the surface of the particles is negatively charged and suggest that the repulsive electrostatic interactions between the particles play an important role in colloid stability of fullerene dispersions.

The size of the fullerene particles depends on the concentration of fullerene in true solution and the type of the fullerene. The concentration dependence of the average size of the colloidal dispersion in acetonitrile is semiquantitatively described by a simple model proposed for the mechanism of the particle formation in the concentration range studied.

The work described in this paper may increase the practical applications of fullerenes, since it suggests an easy way to prepare stable colloidal dispersions of fullerenes containing microcrystals with low polydispersity from a variety of solvent combinations. It may also contribute to better understanding of the solution behavior and solution chemistry of fullerenes.

Acknowledgment. We acknowledge Professor Koki Horikoshi, Japan Marine Science and Technology Center (JAMSTEC), for his continuous support for this work. We thank Dr. Tetsuya Miwa, JAMSTEC, for helpful discussions. Mr. Katsuyuki Uematsu, JAMSTEC, is acknowledged for performing TEM observation of some of the samples. We thank Mr. Keiji Yamazaki (Otsuka Electronics Co., Ltd.) for the help in ELS measurements.

JA010202A

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(42) Ohsawa, Y.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 781−782.

(43) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978−3980.

(44) Sension, R. J.; Szarka, A. Z.; Smith, G. R.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1991**, *185*, 179−183.

(45) Talyzin, A. V. *J. Phys. Chem. B* **1997**, *101*, 9679−9681.

(46) Talyzin, A. V.; Engström, I. *J. Phys. Chem. B* **1998**, *102*, 6477−6481.

(47) *Handbook of Chemistry and Physics*; 76th ed.; CRC Press: Boca Raton, FL, 1995−1996.