



# Comparative analysis of two aqueous-colloidal solutions of C<sub>60</sub> fullerene with help of FTIR reflectance and UV–Vis spectroscopy

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## Abstract

Two types of fullerene–water colloidal systems: molecular-colloidal C<sub>60</sub> solution in water (C<sub>60</sub>FWS) and typical monodisperse C<sub>60</sub> hydrosol are compared in this work. It was confirmed that C<sub>60</sub>FWS consists of isolated C<sub>60</sub> molecules in hydrated state, C<sub>60</sub>@{H<sub>2</sub>O}<sub>n</sub>, and of their small spherical C<sub>60</sub> clusters of different sizes. It was shown that C<sub>60</sub>FWS simultaneously has the properties of both true solutions and colloidal systems. The origin of supramolecular complexes C<sub>60</sub>@{H<sub>2</sub>O}<sub>n</sub> stabilization is explained both by the weak donor–acceptor interactions of unpaired electrons of H<sub>2</sub>O oxygen atoms with fullerene molecule and by formation of ordered, H-bounded and sphere-like hydrated shells around the fullerene. Spectra of surface enhanced infrared absorption (SEIRA) of C<sub>60</sub> on gold substrate were recorded in FTIR reflectance mode. In the 400–900 cm<sup>-1</sup> region some additional vibration bands of C<sub>60</sub>, which are forbidden in IR spectra, have been registered. Earlier the similar bands had been observed in inelastic neutron scattering. © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Fullerenes are widely investigated with the respect to their biological activity, including the following: antioxidant activity, enzyme inhibition, antiviral activity, DNA cleavage, photodynamic therapy, electron transfer, and miscellaneous uses [1,2].

It is well known that fullerenes are not soluble in water [3]. That is why most attention is presently

paid to investigation of biological activity of water soluble C<sub>60</sub> derivatives, which, in turn, can be able to form colloidal solutions. This is especially pertinent to mono-functional fullerene C<sub>60</sub> derivatives [4], which have the tendency to form more or less large particles in concentrated solutions. Such colloidal particles, e.g., ones formed from amino acid C<sub>60</sub> derivatives, have size up to 1–10 μm [5]. This ability of fullerenes and their chemical derivatives to form the colloidal particles in aqueous solution could be used in different ways. For example, they could be used as microsorbents or adjuvants during the process of production and

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testing of a new generation of vaccine for therapy and for prevention of viral infection [6].

On the other hand the  $C_{60}$  molecule could be considered as a colloidal particle itself due to the fact that its diameter equals to 10 Å. This conclusion originates from the traditional point of view that 10-Å border corresponds to the lower border of the colloidal range of dispersity, and the range of true solutions is under this limit [7]. Thus, it is clear that aqueous solutions of any fullerenes must have properties of colloidal systems, which contain associates of solvated fullerenes of different size. Also, it is of very importance that interpretation of molecular mechanisms of fullerene biological activity has to be made taking the aggregate state of fullerenes and their derivatives in aqueous solutions into account.

The present Letter is devoted to the further investigation of two water-colloidal systems of pristine  $C_{60}$ . One of such systems was named by G.V.A. as FWS (fullerene–water–system) and was characterized as an aqueous molecular-colloidal solution, which contains both single fullerene molecules and their fractal clusters in hydrated state [8–10]. In addition to the above-mentioned, the tests of  $C_{60}$ FWS biological activity showed that hydrated fullerenes appeared to be very promising in the context of their biological and therapeutical applications [11]. Especially, it concerns the expressed and positive effects of medicinal and preventive action of microdoses of hydrated fullerenes at the treatments of oncological pathologies [12]. Finally, further investigation of hydrated fullerenes could be useful for explanation of many mechanisms of biological action of fullerenes and their derivatives [2].

The second monodisperse aqueous colloidal system is the typical  $C_{60}$  hydrosol with size of particles of 10 nm [13]. It is called here ‘ChH’.

We had chosen these two colloidal systems,  $C_{60}$ FWS and ChH, for comparative analysis because most of their characteristics are quite similar. These characteristics are: (i) high concentration of fullerenes in water (1 mg/ml and more); (ii) high stability, in the sense that they do not change their properties within six month and more under ambient conditions; (iii) almost identical color of solutions (from pale red to dark brown-red) that

depends on  $C_{60}$  concentration; (iv) negative charge of colloidal particles; (v) preservation of the same properties in the case of dilution or concentrating of both colloidal solutions; (vi) similar ability to coagulate under the inorganic cations influence [13,14].

Also, in this work, comparative analysis of these two colloidal  $C_{60}$  systems is based on new data of FTIR and UV–Vis spectroscopy, as well as on a number of facts, published earlier.

## 2. Materials and methods

For preparation of two fullerene colloids in water we used  $C_{60}$  samples with purity of more than 99.5% and 99.98%, which were obtained from MER Corporation (Tucson, AZ, USA) and ‘TERM’ (Moscow State University, Russia), respectively.  $C_{60}$ FWS was produced without using of any solubilizers and chemical modification [8]. This method is based on transferring of fullerene from organic solution into the aqueous phase with the help of ultrasonic treatment [9]. In different samples of  $C_{60}$ FWS the  $C_{60}$  concentration varied from 0.2 to 2.0 mM (0.14–1.4 mg/ml).

ChH has been obtained using the technology of Wei and co-authors [13] by oxidation of the  $C_{60}$  anion with oxygen in ‘tetrahydrofuran–water’ solutions. For elimination of coarse dispersed particles, the final solution was centrifugated at 7000 rpm and ultrafiltrated with membrane filters with pore size of 0.45 μm ‘Whatman’, England). In ChH the  $C_{60}$  concentration was equal to 1 mg/ml.

For FTIR measurements the drop of  $C_{60}$  colloidal solution (0.02–0.04 ml) was deposited onto substrate and then dried at the room temperature. Then FTIR spectra of  $C_{60}$  precipitates were collected in the reflectance mode with the reflectance attachment on the Bruker IFS-48 instrument in the 380–5300  $\text{cm}^{-1}$  region. The computer program OPUS.2.2 was applied for evaluation of the spectra. It is important, that after drying, the  $C_{60}$  films, deposited from  $C_{60}$ FWS, had soft and plastic properties. In contrast, the  $C_{60}$  films formed from ChH were crystalline and did not give homogeneous layers.

Studying the processes of sorption of water molecules (by the analysis of hydration isotherms) by  $C_{60}$  precipitates was done with piezogravimetry method [15]. We are greatly indebted to Prof. M.A. Semenov and Dr. T.V. Bol'bukh from the Department of Biophysics of Institute of Radiophysics and Electronics of National Academy of Sciences of Ukraine, Kharkov, for piezogravimetry measurements.

### 2.1. SEIRA (surface enhanced infra-red absorbance) effect

Using the metal rough surface as a substrate for studying the adsorbed molecules could lead to the enhancement of FTIR signal in reflectance or attenuated total reflectance modes [16]. The attention to the experimental manifestation of the effect (namely, enhanced intensity of optical transitions in Raman spectra, infrared absorption, luminescence, and generation of the second harmonics at rough metal surface) was paid as early as 20 years ago [17]. The theoretical interpretation of the effect is connected with enhancement of external electric field. It happens due to excitation of local (surface) plasmon vibrations near the essential curvature of rough surface or on metal particles and due to increasing of dipole moment of adsorbed molecules. The estimation shows that the enhancement of the effect is increased in the case when the characteristic size of roughness of the surface is close to 50 Å. In our experiment we used Au–SiO<sub>2</sub> film with thickness of 200 Å and roughness of 50 Å as a substrate.

## 3. Results and discussion

### 3.1. SEIRA experiment

Representative FTIR (SEIRA) spectra of  $C_{60}$  precipitated from  $C_{60}$ FWS and ChH are shown in Fig. 1. Both samples are supposed to have the same surface density of  $C_{60}$ .

For all samples, we observed all the four allowed vibration bands of  $C_{60}$  fullerene [18]. These bands are located at the frequencies 523–526, 571, 1182.5–1183, and 1429  $cm^{-1}$ .

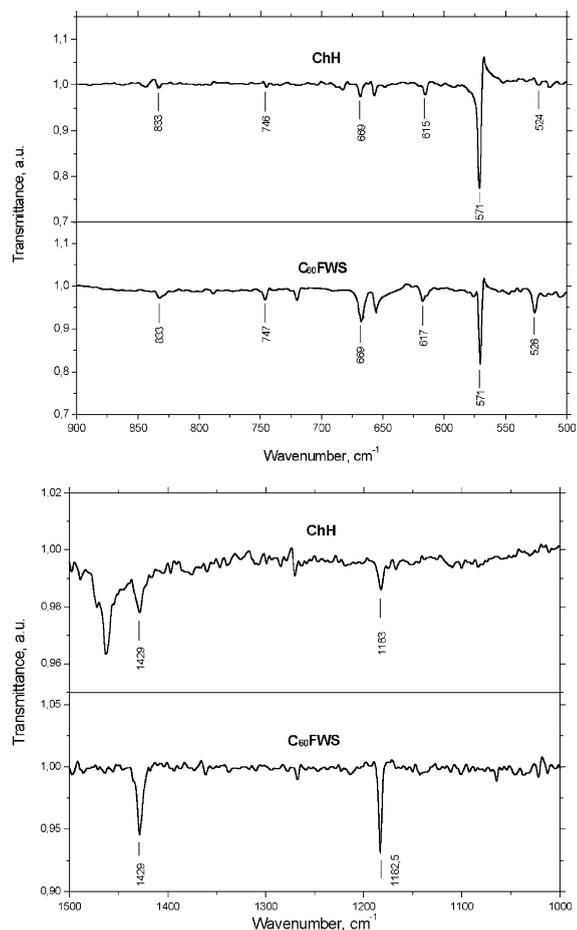


Fig. 1. FTIR (SEIRA) spectra of equal amounts of  $C_{60}$  precipitated from  $C_{60}$ FWS and ChH.

In addition, in the spectra of  $C_{60}$ , precipitated from ChH, the intensive vibration bands have been observed in the regions of 1462–1468  $cm^{-1}$  ( $CH_2$ , asym. bend) as well as at 2849–2851  $cm^{-1}$  ( $CH_2$ , sym. stretch) and 2923–2926  $cm^{-1}$  ( $CH_2$ , asym. stretch) (not shown in Fig. 1). These bands do not disappear after long drying of precipitates from ChH. They correspond to the presence of essential amounts of admixtures of tetrahydrofuran molecules in such samples.

It is important that, for the fullerenes from ChH, the halfwidths of the vibration bands (Table 1) are in 1.2–2.6 times greater than for  $C_{60}$  from FWS. At the same time, the halfwidths of fullerene bands

Table 1  
Halfwidths of  $C_{60}$  bands from two colloidal systems

Frequency ( $\text{cm}^{-1}$ )	Halfwidth ( $\text{cm}^{-1}$ )	
	$C_{60}$ FWS	ChH
524–526	3.9	4.7
571	2.5	3.5
1182.5–1183	2.5	6.5
1429	5.6	9.0

are 2.5–9  $\text{cm}^{-1}$  and they practically do not change during the  $C_{60}$  colloidal solutions drying.

Moreover, after the analysis of FTIR data (Table 1), we have concluded that the widening of the main  $C_{60}$  vibration bands is connected to the strengthening of ' $C_{60}$ – $C_{60}$ ' interactions. Therefore, it is possible to suppose that in colloidal particles

of  $C_{60}$ FWS the interaction between  $C_{60}$  molecules is weaker than those in ChH.

In reflectance spectra of  $C_{60}$ , precipitated onto the gold substrate, we obtained some additional vibration bands in the region 900–400  $\text{cm}^{-1}$ . These bands, which have never been observed earlier in transmittance mode, could be assigned to forbidden in IR spectra vibration modes of  $C_{60}$ . They all have been observed earlier by inelastic neutron scattering [19]. The positions of fullerene vibrational bands are listed in Table 2.

Interestingly, that for fullerene particles from ChH, the number and intensity of additional vibration modes were less than for  $C_{60}$  precipitates from  $C_{60}$ FWS. One of the explanations is that the crystal-like hydrophobic  $C_{60}$  nanoparticles, obtained from ChH, interact weakly with gold sub-

Table 2  
Vibration modes recorded by SEIRA for samples of  $C_{60}$  from two colloidal systems and for  $C_{60}$  powder [18]

Assignment	Frequency ( $\text{cm}^{-1}$ )			Raman scattering	SERS on gold
	Neutron scattering	IR			
		Data received earlier for pure $C_{60}$	Our data SEIRA ( $C_{60}$ on gold)		
$T_{1u}$	531	523	524–526	–	–
$T_{1u}$	572	572	571	–	575
–	620	–	615–617	–	–
–	669	–	669	–	–
$H_g$	708	–	–	710	700
–	740	–	746–747	–	739
$H_g$	773	–	–	774	766
–	837	–	833	–	–
–	877	–	–	–	–
–	919	–	–	–	–
–	960	–	–	–	962
–	1000	–	–	–	–
–	1060	–	–	–	–
$H_g$	1100	–	–	1100	1088
–	1120	–	–	–	–
$T_{1u}$	1180	1180	1182.5–1183	–	–
–	1200	–	–	–	–
$H_g$	1260	–	–	1250	1235
–	–	–	–	–	1307
–	1350	–	–	–	–
–	–	–	–	–	1393
$H_g, T_{1u}$	1420	1430	1429	1430	1422
$A_g$	1480	–	–	1470	1452
$H_g$	1580	–	–	1570	1559

In addition, we present data obtained by other authors with inelastic neutron scattering [19], Raman scattering [18,20] and SERS (surface enhance Raman scattering) [20].

strate, while  $C_{60}$  particles, deposited from FWS, undergo more strong interaction. The possible reason is that  $C_{60}$ FWS consists of more hydrophilic and more small particles ( $\gg 10$  nm, than for ChH).

It is necessary to note that the ability of  $C_{60}$  precipitates from  $C_{60}$ FWS to hold water molecules is much better than that of  $C_{60}$  solid phase from ChH. The last data agree with electron microscopic investigation [10], which has earlier shown that fullerenes from  $C_{60}$ FWS did not lose the sorbed water molecules even in vacuum of  $10^{-5}$  Torr [21].

Taking the above-mentioned facts into account, it is possible to suppose that in FWS the  $C_{60}$  molecules are separated by sorbed water molecules, and fullerenes do not interact directly with each other like  $C_{60}$  molecules in crystal state.

### 3.2. Extraction by organic solvents

Just as for ChH, the simple and important property of  $C_{60}$ FWS is that  $C_{60}$  cannot to be extracted neither by toluene nor by benzene from such aqueous solutions [8]. However, using UV–Vis spectroscopy, we detected that the minimal extraction of  $C_{60}$  is occurred from water-colloidal solutions, and the extent of  $C_{60}$  extraction coincides with solubility of the water in the above-mentioned organic solvents.

Also, in opposite to the ChH properties,  $C_{60}$  from  $C_{60}$ FWS cannot be extracted by toluene in any essential extent in the case when colloidal fullerene particles were precipitated by coagulation of inorganic cations [14].

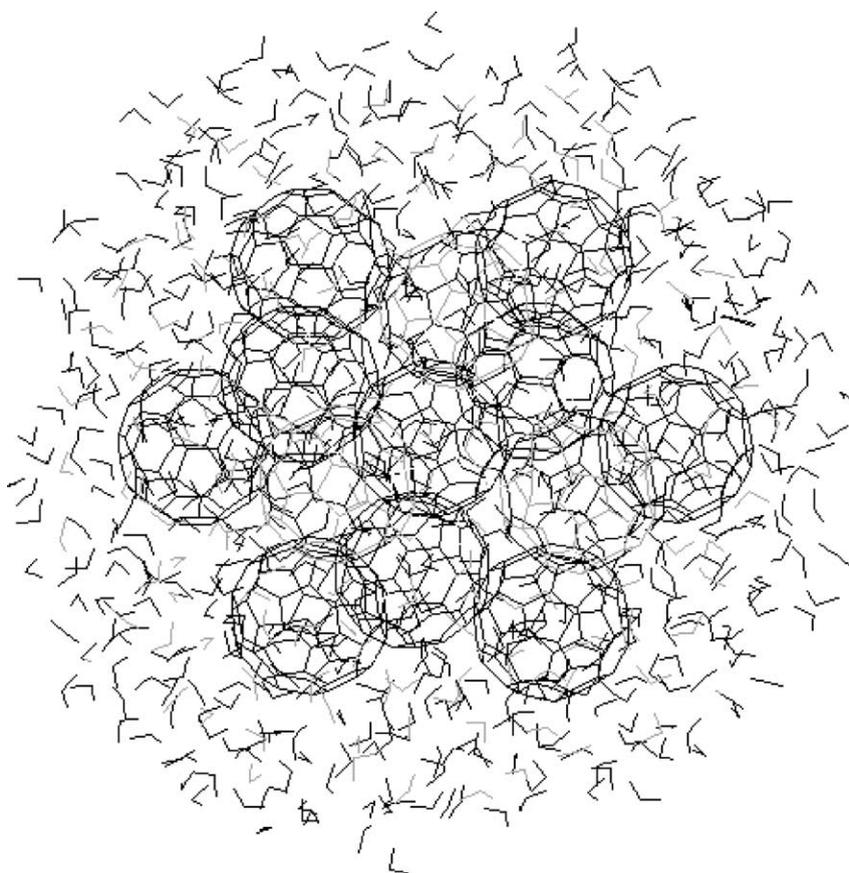


Fig. 2. The predicted model of the elementary spherical (icosahedral) cluster with the diameter of 3.4 nm which consists of 13 hydrated  $C_{60}$  fullerenes.

These facts show that in C<sub>60</sub>FWS the fullerenes are surrounded by the stable hydrophilic shell, which prevents direct interaction of C<sub>60</sub> with hydrophobic molecules of non-polar organic solvents.

### 3.3. Absorption of water molecules by C<sub>60</sub> precipitates

Using the piezogravimetry method, we studied the hydration isotherms of amorphous (uncrystalline) C<sub>60</sub> precipitates obtained by drying of the small droplet of C<sub>60</sub>FWS on quartz crystal. The data received suggest that such precipitates adsorb 5–6 and 20–24 H<sub>2</sub>O molecules per one C<sub>60</sub> molecule when relative humidity (RH) equals to 55% and 85% correspondingly [15]. When the value of RH is more than 85%, the breaking of the resonance ultrasonic oscillations of the quartz crystal is observed due to excessive moistening of C<sub>60</sub> precipitates.

Similar investigations of C<sub>60</sub> precipitates from ChH showed that they absorbed in 3–4 times less water molecules than fullerenes of C<sub>60</sub>FWS. In this case, when RH value became equal to 85%, the loss of the resonance ultrasonic oscillations took place because of shedding of some amount of fullerenes from the surface of quartz crystal due to weak adhesion of fullerene nanocrystals on quartz.

Hence, fullerene particles in C<sub>60</sub>FWS are more hydrophilic and have smaller size (<10 nm), than fullerene particles in ChH.

### 3.4. Transmission electron microscopy (TEM) data

Microscopy of fullerenes from ChH has shown that, after precipitation and drying, the monodisperse C<sub>60</sub> colloidal particles became larger (up to 100 nm); and even under the ultrasonic treatment such precipitates could not be dispersed to primary particles of 10 nm [13].

For fullerenes from C<sub>60</sub>FWS, TEM has showed the big set of very small particles with sizes of 1–4 nm. There is also a set of spherical clusters, diameters of which regularly rise within the range from 7 to 36 nm and are equal to 7.1, 10.9, 14.5, 18.1, 21.8, 25.4, 28.8, 32.4, 36.0 nm [10]. The detailed analysis of large cluster structure showed that they are built up from elementary spherical

(icosahedral [22]) fullerene cluster with the diameter of 3.4 nm. Such cluster consists of 13C<sub>60</sub> molecules and contains water molecules inside (Fig. 2). As it was noted earlier, the form of the large clusters (7–36 nm), consisting of particles of 3.4 nm, can be close to a sphere only if they contain in addition isolated C<sub>60</sub> molecules in a hydrated state [10]. According to the molecular dynamics simulation, the predicted size of such hydrated C<sub>60</sub> is equal to 1.6–1.7 nm<sup>1</sup>, that coincides with the smallest C<sub>60</sub> particle size in C<sub>60</sub>FWS.

It is of interest to note that under the dilution and simultaneous light mechanical shaking of C<sub>60</sub>FWS, the large clusters can dissociate to the small ones [21]. Similar behavior of fullerene's solvates in C<sub>60</sub> benzene solution was observed earlier [23].

In our case, this means that, inside all clusters, C<sub>60</sub> fullerenes are separated from each other by water molecules layers.

### 3.5. UV–Vis spectroscopy

Representative UV–Vis adsorption spectra of C<sub>60</sub> in C<sub>60</sub>FWS, in ChH and in *n*-hexane solution are shown in Fig. 3.

It can be seen that in UV-region the absorbance peculiarities of C<sub>60</sub>FWS are close to the spectrum of C<sub>60</sub> true solution in *n*-hexane [24]. But all absorbance bands of C<sub>60</sub> from FWS are broader and they are shifted to the long-wave range. For example, in *n*-hexane solution we can see the band with  $\lambda_{\max} = 329$  nm ( $\epsilon = 51\,000$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). For C<sub>60</sub>FWS the same band is located at  $\lambda_{\max} = 343$  nm ( $\epsilon = 68\,000$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>).

In contrast to the C<sub>60</sub>FWS, the absorbance bands of C<sub>60</sub> in ChH are broader and less intensive (e.g., for  $\lambda_{\max} = 340$  nm,  $\epsilon = 14\,000$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). Such considerable absorbance bands broadening is typical for colloidal solutions of fullerenes and their chemical derivatives [4,25]. It is stipulated by strong light-scattering effects of C<sub>60</sub> nanoparticles in UV-region.

<sup>1</sup> See, e.g., the computations of professor Martin Chaplin on his www-site (<http://www.sbu.ac.uk/water>, the page 'Aqueous Buckminsterfullerene solutions'). More detailed facts about this will be published hereafter.

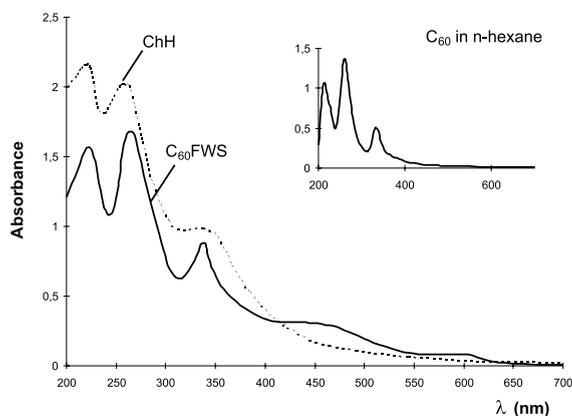


Fig. 3. UV-Vis adsorption spectra of  $C_{60}$  in  $C_{60}$ FWS, ChH and in  $n$ -hexane solution.

These facts, along with FTIR data, testify that  $C_{60}$ FWS consists of much smaller particles ( $\ll 10$  nm) than ChH.

It is important that, in contrast to VIS-absorbance spectra of  $C_{60}$  in  $n$ -hexane and in ChH, the spectrum of  $C_{60}$ FWS has in addition two broad and low-intensive bands, which are located at frequency of 450 nm ( $\epsilon = 21000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and 600 nm ( $\epsilon \sim 4000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). The occurrence of such new absorbance bands in VIS-region is known to be connected with formation of weak donor-acceptor (DA) complexes of  $C_{60}$  with molecules, which are able to be the donors of electrons, e.g., alcohols, aromatic rings, tertiary amines, poly(vinylpyrrolidone) [25,26]. As for water molecule in ' $C_{60}$ - $H_2O$ ' systems, only the oxygen atom can be the donor of electrons during the DA-complexes formation.

It is clear that both in  $C_{60}$ FWS and in ChH colloidal fullerene particles are surrounded by water molecules and interact with them. Namely, the fullerene particles are in hydrated state. The stronger is the hydration (the solvation), the more essential changes in electron spectra of  $C_{60}$  in aqueous solutions must be observed. For fullerenes in organic solvents, the similar solvatochromic effects are well known. Particularly, they are stipulated by formation of weak DA-complexes of  $C_{60}$  with solvent molecules [27].

In this connection, we should remind that in opposite to  $C_{60}$ FWS there are no new long-wave

bands in absorbance spectra of  $C_{60}$  in ChH (Fig. 3). Therefore, in ChH the hydration of typical hydrophobic colloidal  $C_{60}$  nanoparticles, as well as the formation of molecular complexes of ' $\{mC_{60}\} : H_2O$ ' type, does not influence on the electron state of fullerene molecules, which form such  $C_{60}$  nanoparticles. But for  $C_{60}$ FWS the changes in electron spectra of  $C_{60}$  are essential. It can be connected with that the most of single  $C_{60}$  molecules in FWS interact with water molecules due to formation of stable supramolecular complexes of ' $C_{60} : \{H_2O\}_n$ ' type.

The last assumption corresponds to TEM data, which show that a big set of very small particles, with sizes of 1–4 nm, is present in  $C_{60}$ FWS.

In addition to the end of this paragraph, it should be noted that the Beer-Lambert law is strictly valid for the solutions of  $C_{60}$  in different solvent in a wide concentration range (26–5000  $\mu\text{M}$ ) [28]. In our case, for ultramicroheterogeneous(!)  $C_{60}$ FWS [10], the dependence of the optical absorbance from the  $C_{60}$  concentration (3–2200  $\mu\text{M}$  and more) has the linear character also [21].

This fact points out that in  $C_{60}$ FWS, for any spherical clusters of  $C_{60}$  fullerenes with sizes from 3 to 36 nm [10], the optical properties are similar and are stipulated by the properties of the entirely specific supramolecular structure, namely,  $C_{60} : \{H_2O\}_n$ .

So, for such supramolecular complexes, the retention and co-ordination of water molecules at the  $C_{60}$  surface could be caused simultaneously by two reasons:

- (i) the formation of stable spherical shell of interconnected water molecules  $\{H_2O\}_n$ , which, in turn, are joined with each other by H-bonds;
- (ii) the organization of integrated DA-bonds of  $C_{60}$  with oxygen atoms of like water shell,  $\{H_2O\}_n$ .

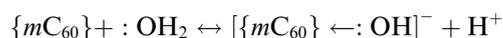
### 3.6. About a nature of the negative charge on the surface of $C_{60}$ colloidal particles

In Section 1, we pointed that the colloidal particles in both ChH and in  $C_{60}$ FWS are negatively charged. As for the nature of the negatively charged surface of colloidal particle, our data on

the threshold for rapid coagulation (TRC) of  $C_{60}$ FWS by cations provide some new considerations concerning our previous assumptions [14]. For example, the TRC value for HCl ( $[H^+] = 0.9$  mM, i.e., at pH 3.05) is much lower than that for KOH ( $[K^+] = 30$  mM, i.e., at pH 12.5), whereas for typical hydrophobic colloids at presence of any univalent inorganic cations the TRC values differ not so considerably [7].

On the whole,  $C_{60}$ FWS is stable in the range of pH 4–12 and at  $-2$  to  $+70$  °C.

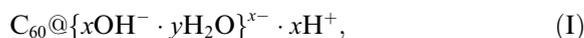
Taking into account that fullerene molecules have not any ionogenic groups, we may assume that a negative charge near the fullerene surface appears due to protolytic processes. The nature of these protolytic processes lies in accordance with the concept of ‘localized hydrolysis’, which was suggested by Robinson and Stokes in the 1950s [29]. In accordance with it, the polarization of water molecules may become stronger near the electron-accepting particles surface. For example, if such colloidal particles consist from fullerene  $C_{60}$  molecules, then the water molecule polarization process (due to of the electron density shift) can be presented as a reaction:



In this case near the hydrated surface of fullerene particle the pH value will be less than 7.

In the recent work of Deguchi et al., the confirmation of such nature of  $C_{60}$  colloids stabilization (in water, in watertetrahydrofuran mixtures and at presence of  $\gamma$ -cyclodextrin) by means of DAcomplexes formation is presented. The reason of this is the charge transfer from oxygen atoms to the fullerenes. Namely, this reason is responsible for negative charge of the fullerene particles surface [30].

Then, taking into account all above-mentioned facts for  $C_{60}$ FWS, the hydrated  $C_{60}$  fullerenes formula,  $C_{60}@H_2O_n$ , can be represented as <sup>2</sup>:



<sup>2</sup> Here the @ symbol is applied by us in compliance with T. Braun recommendations (Editor of ‘Fullerene Science and Technology’ Journal) for a designation of capturer-captive systems [31].

where  $n$  is a number of water molecules, which are in both ionized ( $x$ ) and non-ionized ( $y$ ) state, and  $x + y = n$ .

In aqueous solutions such representation of hydrated fullerenes structure is proved by experiments on titration of  $C_{60}$ FWS with NaOH solutions. In this case the alkali consumption for the titration of free  $CO_2$  dissolved in deionized water was taking into accounted also. In particular, the analysis of typical titration curve (Fig. 4) shows the following.

First, if  $C_{60}$  concentration is equal to  $16 \mu M$ , then the pH of FWS is 4.0. In other words, the relation of  $[H^+]/C_{60}$  is equal to 6. This means that near hydrated fullerenes  $C_{60}$  surface there are six relatively strongly ionized water molecules. Also, on the basis of this titration curve, it was calculated that supramolecular complex (I) has the value of the first ionization stage equal to  $pK_a \sim 3.05$  that coincides with TRC value (at pH 3.05) for HCl. Namely, the coagulation (aggregation) of hydrated  $C_{60}$  fullerenes occurs at such pH values, when the dissociation of polarized water molecules is depressed significantly.

Second, if the part of  $H^+$ -counter ions, e.g., 6, 10, 16, 20 and 36, is substituted by metal ions

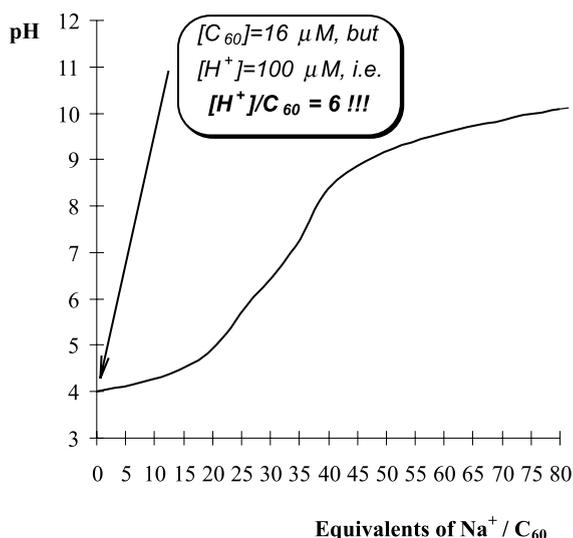


Fig. 4. The changes of acid–basic properties of hydrated  $C_{60}$  fullerenes,  $C_{60}@H_2O_n$ , at the titration of their aqueous solution ( $[C_{60}] = 16 \mu M$ ) by alkali ( $[NaOH] = 10$  mM).

(Na<sup>+</sup>, K<sup>+</sup>, etc.), then the resulting solution will have the pH values 4.1, 4.3, 4.6, 5.1, and 7.3, respectively. Thus, since in hydrated C<sub>60</sub> fullerenes (I) the H<sup>+</sup>-counter ions may be partially replaced by inorganic cations, then C<sub>60</sub>FWS could be considered as a solution of polyelectrolyte, having properties of weak acids.

These facts and the above-mentioned properties of C<sub>60</sub>FWS allow to suppose that such solutions combine simultaneously the properties of colloidal and true solutions. Their properties are very similar to synthetic and natural polymers aqueous solutions.

Therefore, depending on the concentration of C<sub>60</sub> in FWS, the supramolecular complex C<sub>60</sub>@{H<sub>2</sub>O}<sub>n</sub>, as a colloidal particle, can also self-associate and form clusters with different sizes. That is why

- (i) at the TEM-analysis of dried C<sub>60</sub>FWS samples, the great variety of spherical fractal clusters of hydrated fullerenes, (C<sub>60</sub>@{H<sub>2</sub>O}<sub>n</sub>)<sub>m</sub>, has been observed [10] and
- (ii) the existence of (C<sub>60</sub>@{H<sub>2</sub>O}<sub>n</sub>)<sub>m</sub> clusters does not contradict, but prove some typical colloidal properties of C<sub>60</sub>FWS that were described earlier [14,32].

Thus, in opposite to well-known reasons of stabilization of typical colloidal systems [33], including ChH and various C<sub>60</sub> sols [30,34,35], we suppose that one of the main mechanisms of FWS stabilization is the hydration of fullerene molecules with formation of the supramolecular complex of C<sub>60</sub>@{H<sub>2</sub>O}<sub>n</sub> type. In this complex the fullerene molecule is surrounded by the spherical layers of interconnected (H-bounded) water molecules. Along with this, the first water layer is supposed to contain 20–24 H<sub>2</sub>O molecules and, similar to structure of water clusters, proposed earlier by Wei and Castleman [36], the interconnected water molecules of this layer are strongly held on C<sub>60</sub> surface by weak electron donor–acceptor interactions between unpaired electrons of oxygen atoms of H<sub>2</sub>O (the donor) and fullerene molecule (the acceptor).

At present time, the serial experiments, using luminescence spectroscopy, low temperature differential scanning calorimetry and small angle neutron scattering, are held to define more pre-

cisely the number of water molecules (*n*) and to elucidate both structure and properties of the first water layer in hydrated fullerenes, C<sub>60</sub>@{H<sub>2</sub>O}<sub>n</sub>. The results of these experiments will be published hereafter.

#### 4. Conclusions

Based on FTIR and UV–Vis data we confirmed that both C<sub>60</sub>FWS and ChH consist of pristine C<sub>60</sub> fullerene molecules. ChH is typical hydrophobic colloid, whose monodisperse solid phase consists of close to sphere-like C<sub>60</sub> nanocrystals. The size of spherical colloidal particles in C<sub>60</sub>FWS is smaller, up to single C<sub>60</sub> molecules (1 nm), in comparison with particles in ChH (~10 nm). In FTIR-spectra of C<sub>60</sub> fullerene, deposited onto the gold film, we registered additional vibrational modes, which were observed earlier in inelastic neutron scattering spectra only. Also, our analysis confirms the previous conclusion that C<sub>60</sub>FWS is molecular-colloidal solution, which consists of single hydrated C<sub>60</sub> molecules, C<sub>60</sub>@{H<sub>2</sub>O}<sub>n</sub>, and their fractal spherical clusters at the same time [10].

For supramolecular complexes C<sub>60</sub>@{H<sub>2</sub>O}<sub>n</sub>, the origin of their stabilization we explain by the weak donor–acceptor interactions of unpaired electrons of H<sub>2</sub>O oxygen atoms with fullerene molecule and by the formation of the ordered, H-bounded and sphere-like hydrated shells around fullerene's surface.

Properties of FWS combine simultaneously the properties of both colloidal systems and true solutions of weak polyacids or (and) their inorganic salts. Thus, further and deeper investigations of hydrated fullerenes, in which fullerenes are regarded as both molecules and colloidal particles, will permit to find new fundamental contact points between two sciences: science about true solutions and science about colloidal systems.

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