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Towards better understanding of C₆₀ organosols†

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It is of common knowledge that fullerenes form colloids in polar solvents. However, the coagulation via electrolytes and the origin of the negative charge of species are still unexplored. Using a 'radical scavenger' and electrospray ionization spectroscopy (ESI), we proved the formation of ion-radical C₆₀^{•−} and its (probable) transformation into C₆₀^{2−} or (C₆₀)₂^{2−}. The coagulation of C₆₀ organosols by NaClO₄ and other perchlorates and nitrates in acetonitrile and its mixture with benzene obeys the Schulze–Hardy rule. At higher Ca(ClO₄)₂ and La(ClO₄)₃ concentrations, instead of coagulation, stable re-charged colloidal particles appeared, up to a zeta-potential of +(20–42) mV, as compared with −(33–35) mV of the initial organosols. The influence of both HClO₄ and CF₃SO₃H was similar. This phenomenon is attributed to poor solvation of inorganic cations in cationo- and protophobic acetonitrile, which was proven using [2.2.2] cryptand. Further increasing the concentration of Ca(ClO₄)₂ led again to coagulation, thus demonstrating a novel type of 'coagulation zones'.

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1. Introduction

Fullerenes belong to the most-used compounds in various branches of nanotechnology and are intensively studied both experimentally and theoretically.^{1–7} Therefore, it is important to better understand their behavior in a solution. One of the specific features of fullerenes is their ability to form aggregates.^{8–14} While in low-polar aromatic solvents, fullerenes are well solvated and relatively well dissolved,^{14,15} in water they generate hydrosols and suspensions.^{5,11,16–30} In highly polar organic solvents, the molecular solubility of fullerenes is negligible,^{14,15} but they readily form colloidal solutions.^{9–14,31–35}

The state of fullerenes, either molecular or colloidal, in the so-called 'good' or 'strong' solvents, such as CS₂, toluene, and benzene, is still a matter of discussion.^{8,10,11,14,36–40} Some authors

believe that in such a case, aggregates appear only as a result of sonication.¹¹ The aggregates (if any) in 'good' solvents are unstable, destroyed by hand-shaking,⁸ and their formation may be (partly) caused by interaction with oxygen.^{8,38,41} In contrast, in polar or 'poor' organic solvents, the formation of colloidal species is undoubtedly proven.^{9,11–14,31–35} Typical examples are aggregates in *N*-methylpyrrolidin-2-one–acetonitrile mixed solvent,³ toluene (benzene) mixtures with acetonitrile,^{9,12,36} *N*-methylpyrrolidin-2-one^{11,33} and other polar solvents,¹³ DMSO,³¹ acetonitrile, acetone, ethanol, methanol, and other polar solvents.^{32,35,42}

Though the stability and coagulation of aqueous C₆₀ colloids via electrolytes has been examined in full,^{14,16–29,43–49} the corresponding research for organosols is absent to the best of the authors knowledge. Despite numerous publications describing the preparation procedure, particle size and other properties, the coagulation by electrolytes and the origin of the charge of colloidal species in organic solvents yet stays almost unexplored. Herein, we report the regularities of the stability of C₆₀ organosols and the source of the negative charge of aggregates. Moreover, the method of the charge inversion to positive was developed.

In water, the most reliable reason for the negative charging is the adsorption of the HO[−] ions, which may be enhanced by the phenomenon of the 'localized hydrolysis'.^{14,50} It is difficult to imagine, however, analogous influence of the corresponding lyate ions, *e.g.*, CH₂CN[−], in the polar solvents with an ionic product of *ca.* 10^{−30} or less. Then, naturally, the C₆₀ disproportionation resulting in formation of the C₆₀^{•−} species³⁸ or electron transfer from the solvent³² should be assumed; however, the mechanism demands clarification.

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In this study, we report the main regularities of coagulation of C_{60} organosols in a typical polar non-hydrogen bond donor (or 'aprotic') solvent acetonitrile and its mixtures with benzene.

2. Experimental

2.1 Materials

The C_{60} sample (Acros Organics, 99.9%) and 2,6-di-*tert*-butyl-4-methylphenol (Merck, $\geq 99\%$) were used as received. The solvents were purified and dehydrated *via* standard procedures. All perchlorates were synthesized, recrystallized, dried, and kept protected from moisture. Other chemicals were of reagent grade. Triflic acid was a gift from Professor Yu. L. Yagupolskii, Institute for Organic Chemistry, NAS of Ukraine. Cryptand [2.2.2] or Kryptofix 222 (for synthesis) was from Merck, and dicyclohexyl 18-crown-6, *cis-anti-cis*, or isomer B (99.0%) was from the Institute for Physical Chemistry, Russian Academy of Sciences.

2.2 Apparatus

The UV/vis absorption spectra were obtained with the Hitachi U-2000 and SF-46 spectrophotometers against the solvent blanks. The particle size distribution and ζ -potentials were determined *via* dynamic light scattering (DLS) using a Zetasizer Nano ZS Malvern Instrument, scattering angle 173° and a ZetaPALS, Brookhaven Instruments Corporation with scattering angles 90° and 15° for size and ζ measurements, respectively. The DLS data obtained with both instruments coincide. The ζ values, especially in electrolyte-free solutions, were made using the Malvern Instrument; the Smoluchowski equation was applied for processing the data. Electrospray measurements were made using the micrOTOF II Bruker apparatus. For the electron microscopy studies, the Selmi TEM-125K microscope was used. The procedure was as follows. In a vacuum vessel VUP-5M, a 10–20 nm carbon film was deposited from the Volta arc onto freshly cleaved KCl monocrystals at the pressure of residual gases around 10^{-5} Torr. The carbon films were picked up on copper electron microscopy grids. Portions of the examined solutions were deposited on the films and studied after drying in the bright-field and diffraction modes of the TEM at accelerating voltage of 100 kV. The images were registered using a CCD camera or photographic plates.

2.3 Procedure

Normally, after storing in benzene or toluene for about two weeks, the solution was filtered using the $0.45\ \mu\text{m}$ pore sized PTFE filters. The concentrations of the stock solutions in benzene and toluene were determined using the preliminary estimated molar absorptivity values of $64.3 \times 10^3\ \text{M}^{-1}\ \text{cm}^{-1}$ at 335 nm and $58.43 \times 10^3\ \text{M}^{-1}\ \text{cm}^{-1}$ at 336 nm, respectively. Some experiments used either the $6.00 \times 10^{-4}\ \text{M}$ stock solution of C_{60} prepared by dissolving a weighed amount of the solid in benzene or toluene or more concentrated but unsaturated solutions in the same solvents. The aliquots of these stock solutions were added to acetonitrile or other polar solvents at

ambient temperature and all the measurements were made at 25°C . The main working concentration in acetonitrile was $4 \times 10^{-6}\ \text{M}$. At high concentrations, the organosols were less stable. On the other hand, in the benzene–acetonitrile mixtures, higher concentrations of C_{60} were used because of the high electrical resistance of the solutions. In this case, either the $8 \times 10^{-5}\ \text{M}$ C_{60} solution in benzene was mixed with acetonitrile (1:1 by volume) or the stock fullerene solution in benzene was introduced into the C_6H_6 – CH_3CN mixture. All the measurements were numerous repeated and reproduced.

2.4 Determination of the critical coagulation concentration values

During the coagulation studies, two different procedures were used for determining the thresholds of rapid coagulation (critical coagulation concentrations, CCC). The initial concentrated C_{60} solution in an aromatic solvent either was 100-fold diluted by a salt solution in acetonitrile or the 50-fold preliminary diluted C_{60} solution and the electrolyte solutions were mixed. The results were about the same, as well as with the C_{60} concentration of $2.0 \times 10^{-5}\ \text{M}$. In the case of the CCC values that were determined UV-photometrically, the inductive period was assumed to be around 20 min, taking into account the extremely low concentration of the organosol.

3. Results and discussion

3.1 Characterization of the organosols

A number of C_{60} sols were prepared in acetonitrile, DMSO, acetonitrile–DMSO mixed solvent, methanol, as well as in mixtures of toluene or benzene with CH_3CN , DMSO, methanol, and CH_2Cl_2 using, as a rule, the method by Alargova *et al.*³² Absorption spectroscopy, transmission electron microscopy, and dynamic light scattering (Fig. 1) prove the formation of colloidal particles. The electrokinetic potential, ζ , was always negative, and the particle size normally varied within the range from 100 to 600 nm. (In particular, the zeta-potentials of colloidal solutions in salt-free systems should be calculated *via* the Hückel equation, *i.e.*, being 1.5 times higher, but the 'Smoluchowski' values were conventionally used throughout the study.)

The interesting sign of some benzene–acetonitrile solvent systems was the conservation of the fine structure of the C_{60} molecular absorption in the visible zone (Fig. 1a, inset), whereas the DLS data prove the existence of typical colloidal species. Under similar conditions, but with toluene instead of benzene, the smoothing of the visible bands was also not expressed.⁹ This allows for the absence of total adherence of the fullerene molecules at least at the first stage of aggregation in the benzene– CH_3CN solvent. It is in line with the formation of stable C_{60} solvates with benzene in the solid state^{51–53} and with the model of the orientation of the arenes around the C_{60} molecule in a solution.⁵⁴

The sol in acetonitrile was extremely diluted. Considering the 250 nm average particle size, one may estimate the numerical concentration to be about 2×10^{11} particles per dm^3 . Hence, a

Fig. 1 General characterization of the C₆₀ organosols. (a) The absorption spectra of C₆₀ in benzene (solid line), benzene–acetonitrile mixed solvent, 1:1 by volume (dotted line), and in acetonitrile with 1% toluene (dashed line). The optical path length was 0.1 cm (inset: 1 cm). The C₆₀ concentration in benzene and benzene–acetonitrile was 4.02×10^{-5} M. In acetonitrile, the concentration was 4.0×10^{-6} M, and the absorbances were multiplied by 10 before depicting in the figure. (b) The TEM images of the freshly prepared C₆₀ sol in acetonitrile (4.0×10^{-6} M), after evaporating the solvent. (c) The DLS data of the freshly prepared C₆₀ sol (4.0×10^{-6} M) in acetonitrile with 1 vol% toluene; PDI = 0.130 ± 0.015 . (d) The particle size distribution of C₆₀ in a benzene–acetonitrile mixed solvent (1:1 vol ratio, molar fraction of CH₃CN is 0.63), fullerene concentration (4.03 – 4.07×10^{-5} M), freshly prepared; PDI = 0.059 ± 0.013 ; (c, d: 1 – distribution by number, 2 – by intensity and 3 – by volume).

sphere with radius of *ca.* 10 μm corresponds to one colloidal particle. Herein, we shelve the problems of the slow aging of the organosols and slight dependence of properties on the preparation method and focus on the coagulation *via* electrolytes and the source of the particle charge.

3.2 Coagulation by electrolytes

The below results are representative examples from a much larger body of data. The CCCs were determined first

spectrophotometrically (Fig. 2a) and then more precisely with DLS measurements, which provide more obvious and sound data by directly monitoring the particle growth in time (Fig. 2b).

The CCC values were obtained spectrophotometrically in CH₃CN–C₆H₆ mixture (molar ratio 63:37, $\epsilon_r = 12$,⁵⁵ fullerene concentration 4.0×10^{-5} M) and in acetonitrile with 1 vol% toluene (relative permittivity $\epsilon_r = 36$, fullerene concentration 4.0×10^{-6} M). The uncertainty of the CCC was 10% to 25%. For NaClO₄ in the abovementioned solvents, the CCC values of

Fig. 2 Coagulation of the C_{60} organosol by NaClO_4 . (a) The absorbance, A , of the 4.0×10^{-6} M C_{60} sol in acetonitrile at 333 nm vs. time, in the presence of different NaClO_4 quantities: 0 (1); 0.05 mM (2); 0.10 (3); 0.15 (4); 0.20 mM (5). The CCC corresponds to 0.10–0.15 mM NaClO_4 . (b) The size increase of the species in the 4.0×10^{-6} M C_{60} sol in acetonitrile in the presence of different NaClO_4 quantities: 0 (1); 0.01 mM (2); 0.03 (3); 0.05 (4), 0.08 (5, 5'); 0.09 (6); 0.10 (7, 7'); 0.20 (8); 0.30 mM (9). The CCC corresponds to 0.09–0.10 mM NaClO_4 .

1.0 mM and 0.10–0.15 mM, respectively, were obtained *via* UV spectroscopy, whereas for the second case, the DLS indicates $\text{CCC} = (0.09\text{--}0.1)$ mM as being more reliable (hereafter, $1 \text{ mM} = 1 \times 10^{-3} \text{ M}$).

Along with the increase in NaClO_4 concentration, a decrease in the $|\zeta|$ value was observed both in experiments with separately prepared solutions and during electrophoretic titrations (Fig. 3). At 0.10 mM NaClO_4 in CH_3CN , ζ was estimated to be $-(2\text{--}12)$ mV; more precise determination was hindered by the coagulation process.

For $\text{Ca}(\text{ClO}_4)_2$, the CCC value in CH_3CN estimated by spectrophotometry and DLS (Fig. 4) equaled 0.016 and 0.009 mM, respectively.

The data obeys the classical Schulze–Hardy rule for ‘negative’ sols (Table 1). For example, in acetonitrile and benzene–acetonitrile solvents, the CCC^{-1} ratio for Na, Ca, and La perchlorates was 1:(9 to 11):(22 to 66). In the second solvent, the incompleteness of the dissociation of all the salts resulted in much higher CCC values, whereas lanthanum(III) perchlorate is probably incompletely dissociated even in acetonitrile, contrary to NaClO_4 and $\text{Ca}(\text{ClO}_4)_2$.^{56–58} In CH_3CN , the perchlorates of tetra-*n*-butylammonium and cetyltrimethylammonium coagulate the sols half as strong as compared with NaClO_4 , while in the mixed solvent, the situation was reversed.

Fig. 3 Electrophoretic titration of the 4.0×10^{-6} M C_{60} sol in acetonitrile by 0.30 mM NaClO_4 solution in the same solvent; total time of the titration was 2 h.

Fig. 4 The size increase of the species in 4.0×10^{-6} M C_{60} sol in pure acetonitrile (1) and in the presence of different $\text{Ca}(\text{ClO}_4)_2$ quantities: 0.001 (2); 0.004 (3); 0.005 (4), 0.008 (5); 0.01 (6) and 0.15 mM (7).

Table 1 The CCC values/mM [$\pm(10\text{--}25)\%$] of C_{60} in the arene–acetonitrile systems as determined spectrophotometrically^a

Electrolyte	Benzene–acetonitrile, 1:1 (by vol)	Acetonitrile with 6.6 vol% benzene	Acetonitrile with 1 vol% toluene
C_{60} conc./M	4.02×10^{-5}	3.96×10^{-5}	4.0×10^{-6}
NaClO_4	1.00	0.2	0.15
HClO_4	0.80	0.15	0.14
$\text{N}(\text{n-C}_4\text{H}_9)_4\text{ClO}_4$	0.50	—	0.23
$\text{N}(\text{n-C}_{16}\text{H}_{33})(\text{CH}_3)_3\text{ClO}_4$	0.50	—	0.25
$\text{Ca}(\text{ClO}_4)_2$	0.11	—	0.016
$\text{La}(\text{ClO}_4)_3$	0.016	0.003	0.0068

^a Measurements were made at $\lambda = 333$ nm. The CCC values registered after 40 min were *ca.* 1.3–1.7 times lower in both systems.

Three sharp distinctions between the coagulation regularities in acetonitrile and water were observed. First, perchloric and triflic acids exhibited *ca.* the same coagulation strength as NaClO_4 , whereas in the case of the hydrosols HClO_4 , HCl , and HNO_3 acted two orders of magnitude stronger as NaCl .¹⁴

Second, the organosols are inclined to re-charging, *i.e.*, formation of positively charged aggregates, becoming rather stable over time. This phenomenon, atypical for the fullerenes,

was distinctly observed when introducing an excess of multi-charged counter-ions and strong enough acids. Further increasing the salt or acid concentrations coagulated the organosol.

Third, the striking decrease in CCCs in the non-aqueous solvent was fixed: for Na^+ and other single-charged cations, this value was three orders of magnitude lower as compared with those in water.^{14,18–20} Let us consider these issues step by step.

3.3 The origin of the negative charge

In order to clarify the origin of the negative charge, we prepared a set of organosols using benzene–acetonitrile solvent containing the ‘radical scavenger’ 2,6-di-*tert*-butyl-4-methylphenol (ionol). Instead of a rather stable colloid with 150–350 nm-sized species, an immediate jump of the size took place (Fig. 5a), and the ζ value was about $-(10\text{--}15)$ mV instead of $-(30\text{--}35)$ mV. After an hour and a half, the precipitation of larger particles was observed by naked eye, and ζ tended towards zero. (If the experiments with 4×10^{-6} M solution of C_{60} in acetonitrile with 1% toluene were processed, the size increase with ionol occurred much more slowly, but the negative charge of the particles disappeared even quicker. At 2.4×10^{-5} M C_{60} with 6% toluene, the growth of the particles and sedimentation occurred within 3 h, $\zeta = -15$ mV.) The second part of the experiment was also instructive: if ionol was added to the already formed colloidal solution, no rise in size and drop of ζ was registered (Fig. 5a).

The working assumption is as follows. Anion-radicals appear due to either the well-known disproportionation process³⁸ $2\text{C}_{60} \rightarrow \text{C}_{60}^{\bullet-} + \text{C}_{60}^{\bullet+}$ or electron transfer from the solvent,³² e.g., $\text{C}_{60} + \text{CH}_3\text{CN} \rightarrow \text{C}_{60}^{\bullet-} + \text{CH}_3\text{CN}^{\bullet+}$. The high polarity of CH_3CN favors formation of ion-radicals. Then, the anion-radical probably recombines: $2\text{C}_{60}^{\bullet-} \rightarrow \text{C}_{60} + \text{C}_{60}^{2-}$ or $2\text{C}_{60}^{\bullet-} \rightarrow (\text{C}_{60})_2^{2-}$. All the negative species are firmly fixed on the aggregates of fullerene molecules owing to the enormously high electron affinity of the latter. The influence of the ionol may be expressed as follows: $\text{C}_{60}^{\bullet-} + \text{ArOH} \rightarrow \text{C}_{60}\text{H}^- + \text{ArO}^\bullet$; $\text{C}_{60}^{\bullet-} + \text{ArO}^\bullet \rightarrow$ non-radical products. Further decreasing the charge of the colloidal particles in the presence of ionol despite the presence of C_{60}H^- ions may be explained by the interactions of the latter with cationic species, which are also present in the system. Moreover, the H-bond between ArOH and fullerene anions may be formed in the non-hydrogen bond donor solvent acetonitrile.

The initially introduced radical scavenger hinders the first stage, and the aggregates with reduced charge and weakened electrostatic repulsion are unable to overcome the van der Waals attraction. However, when the second stage is completed, the dianions are indifferent to the radical scavenger.

Reasoning from the ζ values at different NaClO_4 concentrations, the interfacial charge may be estimated as one elementary charge per $1 \times 10^3 \text{ nm}^2$ for the sol in CH_3CN (see ESI†). Taking into account the size of the colloidal species, this means that only about

Fig. 5 Behavior of C_{60} in benzene–acetonitrile (1 : 1 by vol) solvent in the presence of 2,6-di-*tert*-butyl-4-methylphenol (ionol). (a) (upper curves) The stock solution of C_{60} in benzene was mixed with acetonitrile containing ionol; the concentrations are 4.0×10^{-5} M and 0.005 M; two separate experiments combined; 1, 2, 3 – by intensity, volume, and number, respectively. (bottom curves) The same sol, but ionol was introduced into the benzene–acetonitrile– C_{60} system at 1.5 h after the preparation of the sol; 1', 2', 3' – by intensity, volume, and number, respectively. (b) The ESI spectrum of $\text{C}_{60}^{\bullet-}$ in benzene–acetonitrile (1 : 1 by vol) solution, fullerene concentration 4.0×10^{-5} M (see also the ESI†).

0.002% of C₆₀ molecules are ionized. It is, therefore, not surprising that we were unable to observe neither a distinct ESR signal of the ion-radicals nor the typical near-IR spectra of the ionic species⁵⁹ in the 10^{-4} – 4×10^{-6} M C₆₀ organosols. However, the electrospray data allowed for registering the C₆₀^{•−} anions (Fig. 5b). Analogous results were obtained with other benzene–CH₃CN compositions. Unfortunately, the ESI spectra were unable to detect the cation-radicals or dications of fullerene, as well as radicals and cations of the solvents. These radical processes are certainly more complicated as compared with the simplified scheme. In the entire benzene solution of C₆₀, the suppressing of radical formation is known to hinder aggregation,³⁸ whereas in polar aprotic (non-hydrogen bond donor) solvents, it results in rapid particle growth.

If the C₆₀ organosol was prepared in a protic solvent, methanol, the ionol displayed no expressed influence on the zeta-potential value (Table 2), though the size of the species decreases (see the ESI†). At the same time, the CCC value in methanol (with 1 vol% toluene) for HClO₄ equals to 1.0 mM, which is much lower as compared with 2.3 mM for NaClO₄, as determined through the spectrophotometric procedure. This situation is closer to that observed in water,¹⁴ wherein the acids display strong coagulative influence (see above). Hence, the negative charge of the colloidal species of C₆₀ in methanol may be caused to some extent by adsorption of methylate ions (ion product of CH₃OH is *ca.* 10^{-17} , much higher than that of acetonitrile), analogous to HO[−] adsorption in the case of hydrosols.

On the other hand, the situation was opposite in the case if the C₆₀ sol was prepared by Deguchi's method of hand-grinding:⁴² the negative charge of the species almost disappears in the presence of the radical scavenger in acetonitrile used in the procedure.

In conclusion, the origin of the negative charge of the colloidal species of C₆₀ in polar non-hydrogen bond donor media is the anion-radical C₆₀^{•−} formation; though after a lapse of time, this species converts into other fullerene anions, which are insensitive to the addition of the radical-scavengers.

The mixing of either the immediately prepared or aged C₆₀ sol in acetonitrile (or in benzene–acetonitrile solvent) with the

solutions of calcium and lanthanum perchlorates results in the re-charging phenomenon considered below.

3.4 Re-charging phenomenon: the influence of multi-charged cations

While at 3.6×10^{-3} mM La(ClO₄)₃ in acetonitrile, the slow coagulation takes place and the zeta-potential became less negative by *ca.* 10 mV, at 0.15 mM La(ClO₄)₃, the positive particles with $\zeta = +(42 \pm 1)$ mV appear (Fig. 6a). Similar results were obtained with calcium perchlorate: the sol with 4×10^{-6} M C₆₀ exhibited ζ values of +20 to +40 mV at Ca(ClO₄)₂ concentrations around 0.15 mM, somewhat depended on the sequence of components mixing and aging of the sol. The same phenomenon was observed by us with Ba(ClO₄)₂. This finding is really surprising, because even the quite predictable formation of interfacial associates, such as La³⁺C₆₀^{2−}, La³⁺(C₆₀)₂^{2−}, and Ca²⁺C₆₀^{2−}Ca²⁺, itself cannot cause the 3- to 7-fold increase in the absolute value of the surface charge density, which may be deduced from the values of the ionic strength and ζ .

Such attraction of cations to the large aggregates of the electrophilic fullerene molecules is a result of poor solvation of Ca²⁺ and La³⁺ in acetonitrile. Indeed, if C₆₀ was introduced into the 0.15 mM Ca(ClO₄)₂ solution with an excess of cryptand [2.2.2], the ζ of the colloidal species dropped to *ca.* +6 mV, and coagulation was observed. Hence, the host (or receptor) organic molecules shelter the inorganic cations from the cationophobic solvent, and the association with the colloidal species becomes needless.

In the case of the colloid prepared according to Deguchi's hand-stirring method,⁴² the same re-charging takes place.

The endohedral metal–fullerene complexes were numerously considered in the literature;⁶⁰ of special interest are the properties of Li⁺@C₆₀ and its reactions in solutions.^{61,62} Some metals form positively charged complexes with C₆₀ and C₇₀ on argon-ion bombardment of fullerenes deposited on a metal substrate,⁶³ and different cationic fullerene-based species, including (fullerene)H⁺, may be formed in the gas phase.⁶⁴ In our case, the interaction of metal cations with C₆₀ molecules in acetonitrile should be considered as a type of exohedral complex formation. For the Li⁺ + C₆₀ system, the recently

Table 2 The values of zeta-potential for C₆₀ colloidal species in different solvents

Solvent system	C ₆₀ conc./M	ζ /mV
Acetonitrile, 1 vol% toluene	4.0×10^{-5}	-34.0 ± 1.8
Acetonitrile, 1 vol% toluene	4×10^{-6}	-33.0 ± 1.4^a
Acetonitrile, 1 vol% toluene + 0.005 M ionol	4×10^{-6}	Around zero
Acetonitrile, prepared by hand-grinding ^b	$>10^{-5}$	-31.0 ± 1.2
Acetonitrile, prepared by hand-grinding ^{b,c}	$>10^{-5}$	≈ -7
Acetonitrile–benzene, 1 : 1 by vol	$(4.02\text{--}4.08) \times 10^{-5}$	-35.1 ± 1.3
Acetonitrile–DMSO–toluene, 50 : 49 : 1 by vol	3.4×10^{-5}	-22.2 ± 1.2
DMSO–toluene, 1 : 1 by vol	3.4×10^{-5}	-16.5 ± 2.5
Methanol, 1 vol% toluene	4×10^{-6}	-21.0 ± 1.3
Methanol, 1 vol% toluene + 0.01 M ionol, 1 h 46 min after preparation	4×10^{-6}	-20.6 ± 1.0

^a In ref. 32, the value $\zeta = -32.5$ mV was reported for C₆₀ in acetonitrile with 0.1 vol% toluene. ^b Prepared according to Deguchi's method.⁴² ^c The same solution, but prepared using ionol-containing acetonitrile.

Fig. 6 (a) The re-charged freshly prepared C₆₀ sol (4.0×10^{-6} M) in acetonitrile, 0.148 mM La(ClO₄)₃; PDI = 0.135 ± 0.044 . (b) The same with 0.15 mM HClO₄; PDI = 0.308 ± 0.004 . (1 – number 2 – intensity 3 – volume). (c) The size increase of the species in the 4.0×10^{-6} M C₆₀ sol in acetonitrile in the presence of different Ca(ClO₄)₂ quantities, mM: 0.15 (1); 0.80 (2); 0.90 (3); 1.0 (4); 5.0 (5); 15 (6); inset: the dependence of the zeta-potential on Ca(ClO₄)₂ concentration. The CCC₂ value corresponds to ≈ 1.0 mM Ca(ClO₄)₂.

published theoretical study predicts charge-induced dipole interaction.⁶⁵

It should be noted that the re-charging occurs even in extremely diluted solutions of acids and calcium perchlorate, contrary to the case with NaClO₄ (see Fig. 3). However, even in the last case, the alteration of the zeta-potential values is partly caused by the Na⁺ adsorption: the ζ value in 0.08 mM NaClO₄ solution became more negative by 5 mV in the presence of 0.2 mM [2.2.2] or dicyclohexyl 18-crown-6.

Thus, it may be summarized that the poor solvation of cations in the cationophobic media results in their excessive attaching to the C₆₀ colloidal species. This leads not only to neutralization of the latter, but even to re-charging them from negative to positive. It should be mentioned, however, that even in the most diluted solutions of the abovementioned salts, the fraction of thus consumed (adsorbed) metal ions is about 1%. Hence, this process is a collateral one for the metal ions in acetonitrile, but plays a decisive role in the fate of the C₆₀ colloids.

The acids also displayed the re-charging effect in acetonitrile.

3.5 Re-charging by acids

In pure acetonitrile, the pK_a values for perchloric and triflic acids were 1.57 and 2.60, respectively.⁶⁶ These electrolytes are also able to re-charge the negative colloidal species of the fullerene in CH₃CN. For instance, $\zeta = +29 \pm 7$ mV at 0.15 mM CF₃SO₃H and even $+37 \pm 3$ mV at the same HClO₄ solution (Fig. 6b). Normally, the C₆₀ colloids re-charged by acids are unstable in time, exhibiting growth of the particles. However, in any case, not only the expected protonation C₆₀²⁻ → HC₆₀⁻ → H₂C₆₀, but also formation of HC₆₀⁺ cations or adsorption of lyonium ions H_{solv}⁺ on fullerene aggregates takes place in this solvent, which is cationo- and protophobic.⁶⁷ Qualitatively similar effects were observed in the benzene–acetonitrile mixed solvent.

Moreover, introduction of the excess of [2.2.2] resulted in a *ca.* zero ζ value and increased size of the particles; the protons were consumed *via* protonation of cryptand, *e.g.*, in the presence of 0.7 mM [2.2.2], the last-mentioned positive ζ value in 0.15 mM HClO₄ returns to the -19 ± 7 mV value.

The weak acid also produces re-charging: the introduction of 350 mM acetic acid in acetonitrile results in a ζ change from -30 to $+8.4 \pm 0.4$ mV and a size increase of the species to ≈ 550 nm.

The acid–base properties of fullerene C₆₀ and relative species were first studied two decades ago. Though the precise determination of a pK_a is a difficult task, the published data^{68–70} allow for predicting the behavior of the C₆₀ molecule and the corresponding anions in the presence of acids. For C₆₀H₂ in DMSO, the following estimates were made by Niyazymbetov *et al.*:⁶⁹ pK_{a1} = 4.7 and pK_{a2} = 16. Cliffl and Bard⁶⁸ studied the radical acidic dissociation in DMSO. They also reported that the protonation of C₆₀²⁻ to C₆₀H₂ in acetonitrile by triflic acid results in a stable orange solution.⁶⁸

While the protonation of fullerene anions is quite predictable, the attachment of protons to the neutral colloidal species in anhydrous acetonitrile is somewhat intriguing. Though only few number of positive charges appear on the aggregates of C₆₀ molecules, it may give evidence for some type of association of the fullerene aggregates with lyonium ions, CH₃CNH⁺. In any case, this issue should be considered in the future, and take into account that earlier the protonated cationic forms of fullerenes were obtained either with superacids⁷¹ or concentrated H₂SO₄.⁷²

As water may also be a source of protons, let us consider the influence of H₂O on the C₆₀ colloid particles.

3.6 The influence of water

Introduction of 2–3 vol% of water to the fullerene colloidal solutions both in acetonitrile and benzene–acetonitrile mixed solvent resulted in a sharp drop of ζ value almost to zero and an increase in the size of the aggregates, whereas the PDI value trended to unity. The same effect was observed for the sol prepared according to Deguchi and Murai.⁴² The evident reason for the effect is the hydrolysis of the charge-determining anions: C₆₀²⁻ → HC₆₀⁻ → H₂C₆₀.

Taking into account the inevitable presence of a small amounts of water (in our dried acetonitrile, it was about 0.005% as determined *via* electrometric Fischer titrations), at least the first step of protonation, $C_{60}^{2-} + H_2O \rightleftharpoons C_{60}H^- + HO^-$, cannot be excluded. The hydroxyl ions, however, are poorly solvated in acetonitrile and this hinders the equilibrium shift towards the products. Addition of much larger amounts of water was considered above. Another way to protonation may be assumed taking into account the additional influence of CO_2 , but CH_3CN as a solvent is also unfavorable for the HCO_3^- anions with localized charge.

However, in the presence of metal cations, especially multi-charged, the anions HO^- and HCO_3^- may be stabilized in tight ionic associates, thus enhancing the ability of water and water + carbon dioxide pair to generate protons. This may even be proposed as a possible mechanism of re-charging the C_{60} aggregates in the presence of metal perchlorates. However, it should be mentioned that the re-charging *via* acids in CH_3CN results in a less stable over time colloidal species as compared with those obtained by $Ca(ClO_4)_2$ and $La(ClO_4)_3$.

In any case, further increasing the concentrations of the La and Ca perchlorates and acids resulted in coagulation caused by compressing the diffuse part of the double electrical layer.

3.7 Second coagulation threshold

For $Ca(ClO_4)_2$, the ≈ 1.0 mM coagulation threshold may be accepted (Fig. 6), which qualitatively agrees with the much higher surface charge density. The latter, in turn, follows from the ζ values at the corresponding salt concentrations.

Thus, in diluted $Ca(ClO_4)_2$ in acetonitrile, the coagulation of fullerene sol occurs ($CCC_1 = 0.009$ mM, value from the DLS data, Fig. 4); at 0.15 mM of the salt, the colloidal particles are already re-charged and stay rather stable even at 0.8 mM $Ca(ClO_4)_2$, whereas the second range of instability begins at $CCC_2 = 0.9$ mM; $CCC_2:CCC_1 \approx 100$. This phenomenon is known in colloid chemistry as 'coagulation zones'. It should be noted that the re-charged particles within the 'plateau' (Fig. 6, inset) are larger in size as compared with the initial organosol.

Though the re-charging phenomenon was numerously repeated and firmly proved by us, it should be a matter of further detailed investigation. For instance, the organosol substantially re-charged by acids is not so stable as compared with that re-charged by Ca^{2+} and La^{3+} , and the effects of the adding of macrocyclic ligands to the $La(ClO_4)_3$ solutions are less expressed, as compared with $Ca(ClO_4)_2$. Moreover, using $La(NO_3)_3$ instead of perchlorate demonstrates minor re-charging and results in coagulation under the same conditions.

3.8 Fullerene organosols vs. hydrosols

Finally, it is rather useful to briefly consider the confrontation of the stability and coagulation of the organosols with those of hydrosols, which exhibit much higher CCCs, based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. Herein, we give only some preliminary remarks.

The numerous and sometimes conflicting results of experimental^{15,14,16–25,43–49} and theoretical^{73–79} investigations demand such a comparison. Indeed, the theoretical calculations often predict strong interaction between C_{60} and water (as a recent example, the work by Choi *et al.*⁷⁷ may be proposed), which may be considered as a type of expressed hydration, whereas the coagulation data indicate the hydrophobic nature of the full-erene hydrosols.

On the other hand, there are two diametrically opposite estimates of the Hamaker constant of fullerene–fullerene interaction, A_{FF} , in vacuum: $A_{FF} = (6.5, \text{ or } 7.5, \text{ or } 8.5) \times 10^{-20} \text{ J}$ ^{14,18,19,21} and $50 \times 10^{-20} \text{ J}$.^{16,17} The first one was obtained from the CCC values of the hydrosol, whereas the second value originates from the data for carbon nanotubes. The DLVO approach in its classical version takes into account the energy of electrostatic repulsion and molecular attraction, the latter being expressed by the combination of Hamaker constants of the solute and solvent. As it was mentioned previously,¹⁴ the A_{FF} value of $50 \times 10^{-20} \text{ J}$ can be accepted if there is some powerful non-DLVO stabilizing factor in the hydrosols, preventing the attraction and coagulation. As such a factor, the abovementioned hydration of C_{60} may be expected.

In this connection, the comparison of the hydrosols with C_{60} organosol in a non-hydrogen bond donor solvent may be helpful. Reasoning from the CCC value for $NaClO_4$ in acetonitrile and the ζ value under the coagulation conditions, the preliminary estimation of $A_{FF} \approx (7–9) \times 10^{-20} \text{ J}$ may be made using a set of constructed Hamaker diagrams. At this stage, we consider the values $(13–15) \times 10^{-20} \text{ J}$ or higher as less probable. Thus, the substantial difference between the CCC values of the 1:1 electrolyte in CH_3CN and water should be attributed to the lower ϵ_r value of the organic solvent (36 *versus* 78 for water) and less negative zeta-potential. Indeed, the coagulation of hydrosols caused by 1:1 electrolytes occurs at $\zeta = -(20–25) \text{ mV}$ or even lower.^{18–20}

Therefore, the strong C_{60} –water interaction, including the charge transfer recently predicted by quantum-chemical calculations,⁷⁷ may in fact result in the enhanced dissociation of water molecules and ensure the substantial negative ζ value of the colloidal species. This is in line with the experimentally revealed adsorption of HO^- ions and the 'localized hydrolysis'. (Note that the polarization of the H_2O molecules near the colloidal species itself cannot cause the electrophoretic effect). In other words, the specific interactions in aqueous media add up to charging the colloidal species.

As for the expressed re-charging effect in water, the $\zeta = +20 \text{ mV}$ was reported for only one $CaCl_2$ concentration, 10^{-4} M , whereas either at lower and higher concentrations or in the case of $BaCl_2$ and $MgCl_2$ solutions, the ζ values were negative.^{16,17} Elimelech and his co-workers also reported less negative ζ values of C_{60} hydrosols with $CaCl_2$ as compared with those in $NaCl$ or KCl solutions, but no re-charging was registered.^{18–20}

It is therefore expected that further study of the coagulation of C_{60} colloids in various polar organic solvents will provide insight into the nature of both organosols and hydrosols.

For instance, our very recent studies show that in methyl alcohol, the C₆₀ colloidal species also underwent re-charging. Namely, in 0.25 mM and 2.5 mM Ca(ClO₄)₂ solutions, $\zeta = +(22-25)$ mV, while the particles became substantially smaller.

4. Conclusions

The source of the negative charge of C₆₀ colloidal aggregates in polar acetonitrile and its mixtures with benzene is from anion-radical formation, as demonstrated using the radical scavenger and the ESI spectra. While the coagulation by NaClO₄ occurs mainly due to the compressing of the diffuse part of the double electrical layer, the multi-charged cations and strong enough acids readily re-charge the colloidal particles. The electrokinetic potential changes gradually from $\zeta = -33$ mV to +30 mV or even somewhat higher. As a result, after the first coagulation threshold, CCC₁, the concentration zone for calcium and lanthanum perchlorates is observed, wherein the organosols are rather stable. Further increasing the electrolyte concentrations again results in coagulation (CCC₂). The revealed phenomenon of soft re-charging of colloidal species of entire C₆₀, which occurs due to the application of the multi-charged cations in the cationophobic solvent without using the oxidizers or voltammetry, may allow governing the movement of species in the electric field. Analogously, pronounced re-charging takes place with perchloric and triflic acids, whereas in acidic media, the colloidal species grew despite obtaining an additional charge. Though only few numbers of positive charges appear on the aggregates of C₆₀ molecules, it may give evidence for protonation of fullerene. An alternative is the adsorption of lyonium ions, CH₃CNH⁺, on the colloidal particles, as a result of poor solvation of cations in the bulk phase. In any case, it should be kept in mind that the total C₆₀ concentration in the systems under study was as low as 4×10^{-6} to 4×10^{-5} M and only ca. 0.002% of all the fullerene molecules underwent ionization and participated in the ionic processes.

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