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## PROPERTIES OF THE FULLERENE C<sub>60</sub> COLLOID SOLUTIONS IN ACETONITRILE AS PREPARED BY DEGUCHI'S HAND-GRINDING METHOD

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In this communication, we describe some colloidal properties of the fullerene C<sub>60</sub> organosol in acetonitrile, prepared using the Deguchi's hand-grinding technique. The negatively charged colloidal particles with zeta potential about -30 mV possess the size of 200–300 nm, as determined using the dynamic light scattering method. The transmission electron microscopy images confirm these estimates. The origin of the negative charge of the colloidal species is ascribed to the formation and re-combination of free radicals; in the presence of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol, the colloidal system appeared to be more polydispersed and the species exhibited a substantially less negative zeta-potential. The coagulation via electrolytes has been registered using the UV-spectroscopy and dynamic light scattering. In the presence of inorganic cations, especially hydrogen ions and double-charged calcium ions, the colloidal particles are readily re-charged, and the zeta-potential becomes substantially positive.

**Key words:** fullerene C<sub>60</sub>, colloid solution, acetonitrile, dynamic light scattering, zeta-potential, re-charging of particles.

### Introduction

Though fullerenes are sparingly soluble in any organic liquids, their solubility in polar solvents is unusually low [1, 2]. However, the colloidal solutions, i.e., organosols, are readily formed on introducing the fullerene solutions in benzene, toluene, or CS<sub>2</sub> into acetonitrile, acetone, methyl or ethyl alcohol, etc. [2–11]. This general approach to preparation is well known and named 'the method of physical condensation' in textbooks for colloid chemistry [12]. Another general method, the 'dispersion', or 'top-down' preparation of colloids, is said to be applicable to manufacturing only rather large-sized dispersed systems, i.e., suspensions. However, as it was demonstrated recently by Deguchi et al., the five-minute hand-grinding of the solid C<sub>60</sub> in the agate mortar and further sonication in the corresponding liquid allows obtaining nano-sized colloidal particles both in organic solvents [8] and in water [13]. The reason is the specificity of the crystal structure of the solid fullerene [13].

Our recent study [14] has been devoted to the C<sub>60</sub> colloidal solution in acetonitrile obtained by the method proposed by Alargova et al. [6].

The present study was undertaken in order to obtain some more details concerning the properties of thus obtained C<sub>60</sub> sol in acetonitrile, because this system was described less detailed [2] as compared with the aqueous colloid solution prepared using the above-mentioned 'engineering of antiquity' [13].

### Experimental

**Materials.** The C<sub>60</sub> sample (Acros Organics, 99.9%) and the 2,6-di-*tert*-butyl-4-methylphenol (Merck, ≥ 99 %) were used as received. Acetonitrile has been purified and dehydrated via standard procedures. The perchlorates have been synthesized, re-crystallized, dried, and kept protected from moisture. Other chemicals were of reagent grade.

**Apparatus.** The UV/vis absorption spectra were measured with the Hitachi U-2000 and SF-46 spectrophotometers against the solvent blanks. The particle size distribution and zeta-potentials were determined via dynamic light scattering (DLS) using Zetasizer Nano ZS Malvern Instruments apparatus, scattering angle was 173°. The measurements have been made at 25°C.

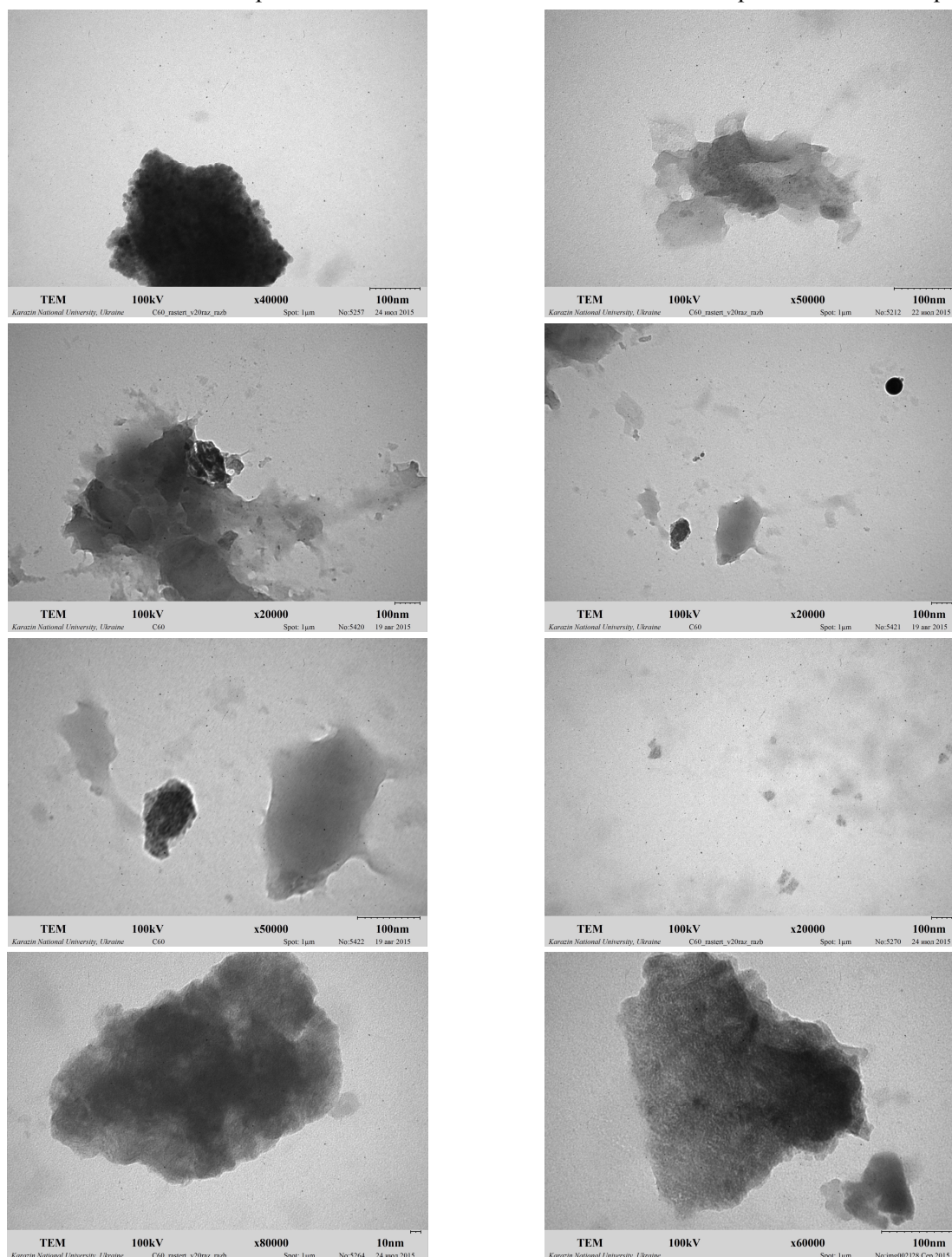
For the electron microscopy studies, the Selmi TEM-125K microscope was used. The procedure was as follows. In a vacuum vessel VUP-5M, a 10–20 nm carbon film was deposited from the Volta arc on fresh cleavages of KCl monocrystals at the pressure of residual gases around 10<sup>-5</sup> Torr. After floating off in distilled water and drying, the carbon films were picked up on copper electron-microscopy grids. The portions of the examined solutions were deposited on the films and studied

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after drying in the bright-field and diffraction modes of the TEM at accelerating voltage of 100 kV. The images were registered using the CCD camera.

### Results and Discussion

**Preparation and Characterisation of the Organosol.** The procedure recommended by Deguchi and Mukai [8] has been repeated numerously; the mass of C<sub>60</sub> for the grinding during 5 min in the agate mortar was 2 to 3 mg. After adding acetonitrile, the sonication has been carried out in the apparatus with electrical power ca. 50 W and frequency 40 kHz. The duration of the ultrasound treatment has been varied in a set of experiments. The undissolved residue has been separated from the liquid.

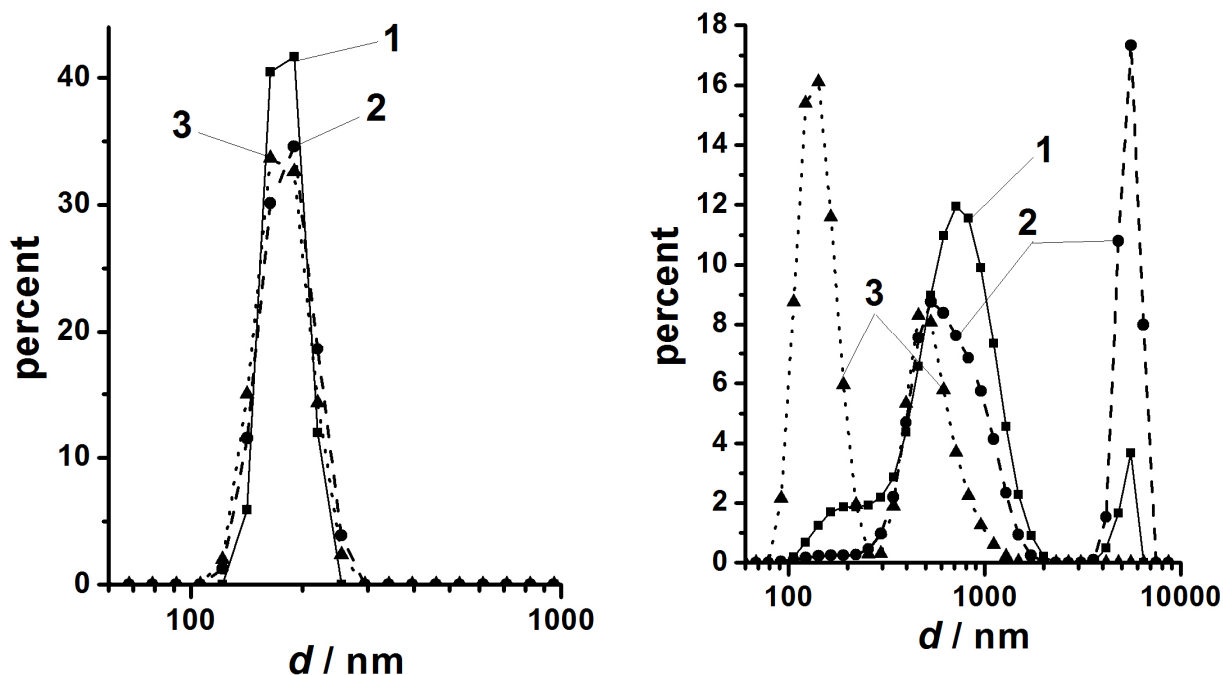


**Figure 1.** The TEM images of two independently prepared samples of C<sub>60</sub> colloid, after evaporation of the 3-fold diluted solutions.

The transmission electron microscopy images are exemplified in Figure 1. The results of the DLS measurements are shown in Fig. 2. As a rule, the particle size depends to some extent on the conditions of sonication (Table 1).

The results of TEM and DLS examination agree in outline with those published by Deguchi and Murai; in acetonitrile, the particle size was reported as 229 nm [8].

Though the colloidal particles are always negative, the zeta-potential value varies along with the total time and regime of the ultrasound treatment.



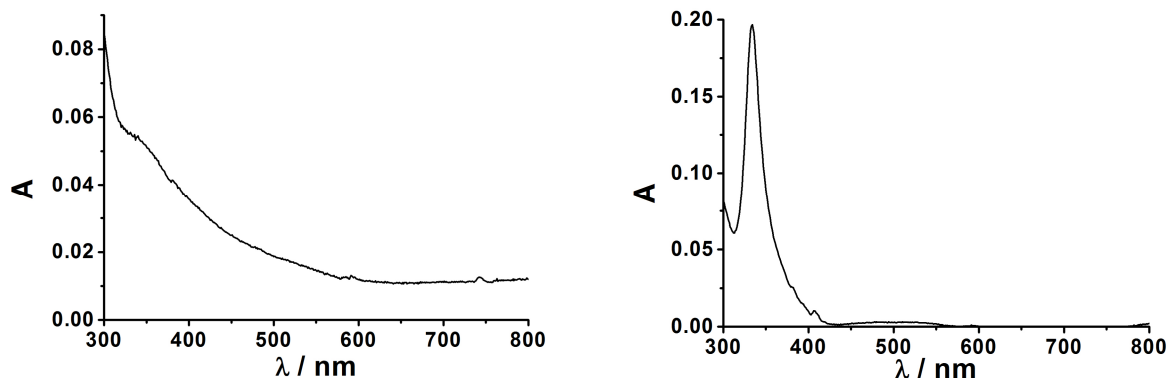
**Figure 2.** The typical size distributions. Left: prepared after 1.5 h sonication. Right: after 8 min sonication; distribution by intensity (1); by volume (2), by number (3).

The sonication conditions markedly influence the features of the colloidal system. For example, if the sonication continues only 8 to 16 min, the system contains not only 100–300 nm particles, but also larger ones, around micron-sized, which remain after additional sonication after one day. By contrast, after 40 min of permanent sonication, such large particles do not appear. The mean value of the zeta-potential estimated for seven independently prepared colloids is  $\zeta = -31 \pm 12$  mV, whereas the same value for the 40 minute-sonicated colloid is  $\zeta = -30 \pm 2$  mV (Smoluchowski equation was used).

**Table 1.** The characterization of the C<sub>60</sub> colloid in acetonitrile

Parameter	Experiment number				
	I	II	III	IV	V
$d$ (by number)/nm	$273 \pm 5$	$194 \pm 4$	$196 \pm 4$	$200 \pm 3$	$179 \pm 12$
$d$ (by volume)/nm	$296 \pm 8$	$204 \pm 6$	$247 \pm 6$	$221 \pm 4$	$184 \pm 13$
$d$ (by intensity)/nm	$280 \pm 6$	$197 \pm 5$	$218 \pm 3$	$208 \pm 3$	$180 \pm 12$
PDI	$0.264 \pm 0.009$	$0.297 \pm 0.029$	$0.219 \pm 0.012$	$0.183 \pm 0.007$	$0.483 \pm 0.037$
$\zeta$ /mV	$-31 \pm 1$ mV	$-28 \pm 3$	$-41.9 \pm 0.2$	$-31 \pm 4$	$-29.3 \pm 0.6$
Sonication mode	ca. 60 min, with 7 inter- vals	40 min	240 min	90 min	90 min

The UV-vis spectrum of the colloid solution obtained via hand-grinding is monotonous, without distinct maxima (Figure 3, left).



**Figure 3.** The absorption spectra of C<sub>60</sub> colloid in acetonitrile, obtained by the ‘stirring’ procedure and additionally diluted (left) and the solution V (see Table 1) diluted 10-fold by benzene (right).

In order to estimate the concentration, the initial colloidal solution was diluted ten-fold by benzene. The UV spectrum was measured after one week (Figure 3, right). The absorption maximum was registered at 334 nm; the concentration was calculated using the molar absorptivity value of  $64.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ , previously determined at 335 nm in pure benzene. (Deguchi and Murai carried out this procedure using toluene.) For instance, the total fullerene concentration in system V was  $3.06 \times 10^{-5} \text{ M}$ . For further studies, the initial solutions were diluted by acetonitrile; hereafter, the concentrations of the working colloidal solutions are expressed formally in the molar scale.

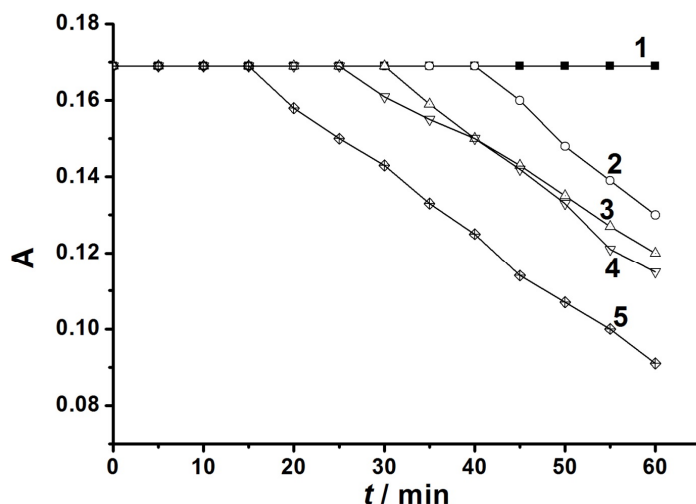
**The origin of the negative charge of the colloidal species.** Contrary to hydrosols, where the negative charge of colloidal species is most probably caused by the adsorption of HO<sup>-</sup> ions, enhanced by the localized hydrolysis [2, 15], in acetonitrile such process, either due to the presence of CH<sub>2</sub>CN<sup>-</sup> ions or water traces, is less probable. However, if the organosol has been prepared with acetonitrile which contained 2,6-di-tert-butyl-4-methylphenol (ionol), the zeta-potential was substantially less negative,  $\zeta \approx -7 \text{ mV}$ , and the system becomes highly polydispersed. This reveals the ion-radical origin of the negative charge in acetonitrile. Probably, anion-radicals appear thanks either to the well-known disproportionation process  $2\text{C}_{60} \rightarrow \text{C}_{60}^{\bullet-} + \text{C}_{60}^{\bullet+}$  or electron transfer from the solvent, e.g.,  $\text{C}_{60} + \text{CH}_3\text{CN} \rightarrow \text{C}_{60}^{\bullet-} + \text{CH}_3\text{CN}^{\bullet+}$ , as it was supposed recently for the C<sub>60</sub> organosol prepared by the physical condensation method [14]. Then the anion-radicals probably re-combine:  $2\text{C}_{60}^{\bullet-} \rightarrow \text{C}_{60} + \text{C}_{60}^{2-}$  or  $2\text{C}_{60}^{\bullet-} \rightarrow (\text{C}_{60})_2^{2-}$ . The influence of the ionol may be expressed as follows:  $\text{C}_{60}^{\bullet-} + \text{ArOH} \rightarrow \text{C}_{60}\text{H}^- + \text{ArO}^\bullet$ ;  $\text{C}_{60}^{\bullet-} + \text{ArO}^\bullet \rightarrow \text{non-radical products}$ . Further decrease in the charge of the colloidal particles in the presence of ionol despite the presence of C<sub>60</sub>H<sup>-</sup> ions may be explained by the interactions of the latter with cationic species, which are also present in the system in accord to the electroneutrality principle.

Addition of 1 vol. % water to stored system II results in immediate disappearance of the negative charge of the colloidal species:  $\zeta$  changes from  $-28 \pm 3 \text{ mV}$  to  $+2.9 \pm 0.8 \text{ mV}$ . The evident reason is the hydrolysis ( $\text{C}_{60}^{2-} + \text{H}_2\text{O} \rightarrow \text{C}_{60}\text{H}^- \rightarrow \text{C}_{60}\text{H}_2$ ) and probably even additional adsorption of some small amounts of hydronium ions on the surface of the particles. Moreover, even in dry acetonitrile the re-charging appeared to be a quite typical phenomenon.

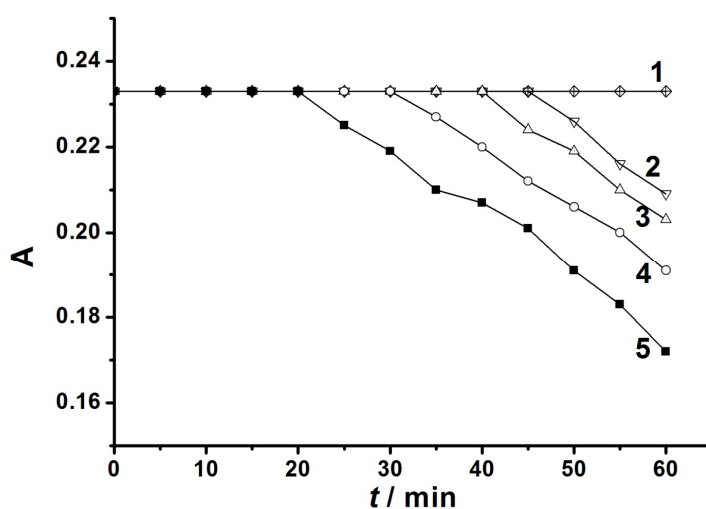
**The interaction with electrolytes.** First, the principal change (breakup) of the colloid system was registered using the UV spectra (Figures 4 and 5).

The evident changes occur at concentrations  $2.4 \times 10^{-3}$ ,  $2.75 \times 10^{-3}$ , and  $2.5 \times 10^{-3} \text{ M}$  for NaClO<sub>4</sub>, tetra-*n*-butylammonium and cetyltrimethylammonium perchlorates respectively. These values may be considered as the critical concentrations of coagulation (CCC). For La(ClO<sub>4</sub>)<sub>3</sub>, the analogously estimated CCC =  $5.0 \times 10^{-5} \text{ M}$  value agrees with the Schulze–Hardy rule.

The results of UV spectra observations for other electrolytes need more detailed consideration. So, the alterations of absorbance became evident at  $2.0 \times 10^{-3}$  M for  $\text{HClO}_4$ , while in the presence of the perchloric acid, the charge inversion of the colloidal species up to  $\zeta = +22$  mV at  $5.0 \times 10^{-3}$  M  $\text{HClO}_4$  takes place. Also, the DLS data demonstrate that at such  $\text{NaClO}_4$  concentrations the increase in the size of colloidal particles up to microns takes place. [All the UV and DLS measurements have been made at  $C_{60}$  content of  $(4-6) \times 10^{-6}$  M.]



**Figure 4.** The time dependence of absorbance of the  $6 \times 10^{-6}$  M  $C_{60}$  solution at 333 nm at different  $\text{NaClO}_4$  concentrations: without addition (1); 0.001 M  $\text{NaClO}_4$ , (2); 0.0015 M (3); 0.002 M (4); 0.0025 M  $\text{NaClO}_4$  (5).



**Figure 5.** The time dependence of absorbance of the  $6 \times 10^{-6}$  M  $C_{60}$  solution at 333 nm at different  $\text{La}(\text{ClO}_4)_3$  concentrations: without addition (1);  $2 \times 10^{-5}$  M  $\text{La}(\text{ClO}_4)_3$  (2);  $3 \times 10^{-5}$  M (3);  $4 \times 10^{-5}$  M (4);  $5 \times 10^{-5}$  M  $\text{La}(\text{ClO}_4)_3$  (5).

But the UV-spectral data appeared to be somewhat ambiguous. Indeed, the absorption decrease near 333 nm is observed at  $\text{Ca}(\text{ClO}_4)_2$ , concentration of  $2.5 \times 10^{-3}$  M, whereas at  $1.3 \times 10^{-6}$  M  $\text{Ca}(\text{ClO}_4)_2$  the zeta-potential is much less negative as compared with the data in Table 1:  $\zeta = -8$  mV, whereas at  $5.0 \times 10^{-6}$  to  $5.0 \times 10^{-4}$  M  $\text{Ca}(\text{ClO}_4)_2$  the  $\zeta$  values are positive with the mean value of +29 mV. Hence, the size increase observed at  $2.5 \times 10^{-3}$  M corresponds to the breakup of the already changed sol, which differs from the initial one. Some re-charging of the colloidal species has been registered also in the presence of  $\text{NaClO}_4$ . For instance, at  $1.0 \times 10^{-4}$ ,  $1.0 \times 10^{-3}$ , and  $(2.5-2.8) \times 10^{-3}$  M  $\text{NaClO}_4$ , the values  $\zeta = -17.2$ , +6.2, and +8.6 mV respectively have been determined (mean values of

two experimental series). Unfortunately, the zeta-potential values for the independently prepared sols at the same salt concentration may vary substantially, though the phenomenon of re-charging, previously observed in the experiments with the C<sub>60</sub> sol in acetonitrile prepared by the condensation method [14], is certainly confirmed with the ‘hand-grinded’ C<sub>60</sub> in the present study. The main reason is probably the poor solvation of cations in cationo- and protophobic solvent acetonitrile [16, 17].

Also, it should be noted that the CCC values for the C<sub>60</sub> organosol prepared by the ‘hand-grinding’ are substantially higher as compared with those obtained via the same UV-spectroscopy method for the sol in acetonitrile prepared by the condensation procedure [14]. Interestingly, the CCC value for the hydrosol prepared by stirring of the solid C<sub>60</sub> in water is also higher than that for the colloidal system obtained by transition of fullerene from toluene into water [18].

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Н. О. Мчедлов-Петросян, Ю. Т. М. Аль-Шуучи, Н. Н. Камнева, А. И. Марынин, А. П. Крыштал. Свойства коллоидных растворов фуллерена C<sub>60</sub> в ацетонитриле, приготовленных методом ручного растирания по Дегучи.

Отрицательно заряженные частицы со значением зета-потенциала около  $-30$  мВ имеют, по данным динамического рассеяния света, размер  $200-300$  нм, что подтверждается и методом просвечивающей электронной микроскопии. Вероятной причиной возникновения отрицательного заряда коллоидных частиц является образование и последующая рекомбинация анион-радикалов фуллерена, поскольку в присутствии ловушки свободных радикалов 2,6-ди-трет-бутил-4-метилфенола образующаяся коллоидная система характеризуется высокой полидисперсностью, а зета-потенциал частиц гораздо менее отрицателен. Коагуляция органозоля исследована методами УФ-спектроскопии и динамического рассеяния света. В присутствии неорганических катионов, особенно ионов водорода и двухзарядных ионов кальция, частицы проявляют склонность к перезарядке, о чем свидетельствуют существенно положительные значения зета-потенциала.

**Ключевые слова:** фуллерен  $C_{60}$ , коллоидный раствор, ацетонитрил, динамическое рассеяние света, зета-потенциал, перезарядка частиц.

М. О. Мчедлов-Петросян, Ю. Т. М. Аль-Шуучи, Н. М. Камнева, А. І. Маринін, О. П. Криштал. Властивості колоїдних розчинів фуллерена  $C_{60}$  в ацетонітрилі, виготовлених методом ручного розтирання за Дегучі.

Негативно заряджені частинки зі значенням зета-потенціалу близько  $-30$  мВ мають, за даними розсіювання світла, розмір  $200-300$  нм, що підтверджується і методом просвічуючої електронної мікроскопії. Ймовірною причиною виникнення негативного заряду колоїдних частинок є створення та подальша рекомбінація аніон-радикалів, оскільки в присутності «прибиральника» вільних радикалів, 2,6-ди-трет-бутил-4-метилфенола, колоїдна система характеризується високою полідисперсністю, а зета-потенціал значно менш негативний. Коагуляція органозоля досліджена методами УФ-спектроскопії та динамічного розсіювання світла. В присутності неорганічних катіонів, особливо іонів водню та двозарядних іонів кальцію, частинки проявляють схильність до перезарядження, про що свідчать суттєво позитивні значення зета-потенціалу.

**Ключові слова:** фуллерен  $C_{60}$ , колоїдний розчин, ацетонітрил, динамічне розсіювання світла, зета-потенціал, перезарядження частинок.

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