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Dependence of the dimension of the associates of water-soluble tris-malonate of light fullerene – $C_{60}[=C(COOH)_2]_3$ in water solutions at 25 °C

K. N. Semenov[1], N. A. Charykov[2,3], A. S. Kritchenkov[1], I. A. Cherepkova[2], O. S. Manyakina[2], D. P. Tyurin[2], A. A. Shestopalova[2], V. A. Keskinov[2], K. V. Ivanova[2], N. M. Ivanova[1], D. G. Letenko[4], V. A. Nikitin[5], E. L. Fokina[1], M. S. Gutenev[5]

[1]St. Petersburg State University, Saint-Petersburg, Russia
[2]St. Petersburg State Technological Institute (Technical University), Saint-Petersburg, Russia
[3]St. Petersburg State Electro-Technical University (LETI), Saint-Petersburg, Russia
[4]St. Petersburg State University of Architecture and Civil Engineering, Saint-Petersburg, Russia
[5]Peter the Great St. Petersburg Polytechnic University, Saint-Petersburg, Russia

keskinov@mail.ru

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Investigation of the concentration dependence of the size and type $C_{60}[=C(COOH)_2]_3$ aggregation in aqueous solutions at 25 °C was accomplished with the help of a dynamic light scattering method. It was determined that three types of aggregates are realized in the solutions. The average number of $C_{60}[=C(COOH)_2]_3$ molecules in smaller aggregates and all types of aggregates were calculated. One can see that over the whole concentration range, from 0.01 to 10 g/dm^3, aqueous solutions of $C_{60}[=C(COOH)_2]_3$ are characterized by sub-micro-heterogeneous behavior (because second-type aggregates with the linear dimensions – hundreds of nm are formed in all solutions). Additionally, the most concentrated solution ($C = 10$ g/dm^3) is characterized by micro-heterogeneous or colloid behavior (because third-type aggregates with the linear dimensions on the order of μm – are formed). In order to describe or explain such behavior, a stepwise aggregation model was invoked.

Keywords: tris-malonate of light fullerene, method of the dynamic light scattering.

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1. Introduction

This article further develops investigations which were initiated previously [1–4]. These studies were devoted to the synthesis and identification of tris-malonate $C_{60}[=C(COOH)_2]_3$ [1] (the original synthesis of this water soluble derivative was described earlier in [5]), the investigation of volume and refraction properties of its aqueous solutions at 25 °C [2], poly-thermal solubility and complex thermal analysis [3], concentration dependence of electric conductivity and hydrogen ion concentration for aqueous solutions [4]. This study was undertaken to investigate the concentration dependence of $C_{60}[=C(COOH)_2]_3$ aggregate sizes in aqueous solutions at 25 °C, and as in the earlier article [3], these studies to investigate the state of $C_{60}[=C(COOH)_2]_3$ and its aggregation processes were performed in aqueous solutions over a wide concentration range – 0.1 ÷ 10 g/dm^3.

TABLE 1. Linear dimensions of C_{60}[=C(COOH)$_2$]$_3$ aggregates in aqueous solutions at 25 °C

Concentration of C_{60} tris-malonate C (g/l)	Diameter of monomer $\bar{d}_0 \approx 1.8$ nm (nm)	Diameter of first type associates d_1-interval ($\bar{d}_1$) (nm)	Diameter of second type associates d_2-interval ($\bar{d}_2$) (nm)	Diameter of third type associates d_3-interval ($\bar{d}_3$) (nm)
0.01	No effect	30–70 (50)	200–400 (300)	No effect
0.1	No effect	40–80 (60)	300–500 (400)	No effect
1.0	No effect	40–80 (60)	300–500 (400)	No effect
5.0	No effect	40–80 (60)	300–500 (400)	No effect
10.0	No effect	40–80 (60)	500–1000 (750)	4000–6000 (5000)
Concentration of C_{60} tris-malonate C (g/l)	Average number of monomer molecular of C_{60} tris-malonate in clusters of the first order $N_{0\to1}$ (units)	Average number of clusters of the first order in clusters of the second order $N_{1\to2}$ (units)	Average number of clusters of the second order in clusters of the third order $N_{2\to3}$ (units)	
0.01	$1.1 \cdot 10^4$	$1.1 \cdot 10^2$	No effect	
0.1	$1.9 \cdot 10^4$	$1.6 \cdot 10^2$	No effect	
1.0	$1.9 \cdot 10^4$	$1.6 \cdot 10^2$	No effect	
5.0	$1.9 \cdot 10^4$	$1.6 \cdot 10^2$	No effect	
10.0	$1.9 \cdot 10^4$	$1.0 \cdot 10^3$	$1.6 \cdot 10^2$	

2. Dimension of the associates of C_{60}[=C(COOH)$_2$]$_3$ in water solutions at 25 °C

To investigate the concentration dependence of C_{60}[=C(COOH)$_2$]$_3$ aggregate size in aqueous solutions at 25 °C, we utilized a dynamic light scattering method in the visible wavelength region. The Malvern Zeta Nanosizer device was used. Data are represented in Table 1 and Fig. 1 and 2 (as the examples).

To estimate the linear size of the C_{60}[=C(COOH)$_2$]$_3$ monomer, $d_0(monomer)$ was obtained from the refraction data [2]. Molar refraction of C_{60} tris-malonate $R_{tris-malonate} \approx 201$ cm^3/mole, so: $R_{tris-malonate} \approx 2.01 \cdot 10^{-4}/6.02 \cdot 10^{23} \approx 3.0 \cdot 10^{-27}$ m^3/molecule, so: in the spherical approximation, the linear dimension: $d_0(monomer) \approx [18/\pi \cdot 10^{-27}]^{1/3} \approx 1.8 \cdot 10^{-9}$ m $= 1.8$ nm.

3. Number of i-th type associates packed into $(i+1)$-th type associates

The number of i-th type aggregates packed into $(i+1)$-th type aggregates – $N_{i\to i+1}$ was estimated by the following equation:

$$N_{i\to i+1} = (d_{i+1}/d_i)^3 \cdot K_{pack}, \tag{1}$$

where: $K_{pack} \approx 0.52$ – is formal pack coefficients for the case of 'little spheres', packed in the 'larger sphere' ($1 - K_{pack} \approx 0.48$ – volume fraction, which is empty of is fulfilled by a molecular of H_2O).

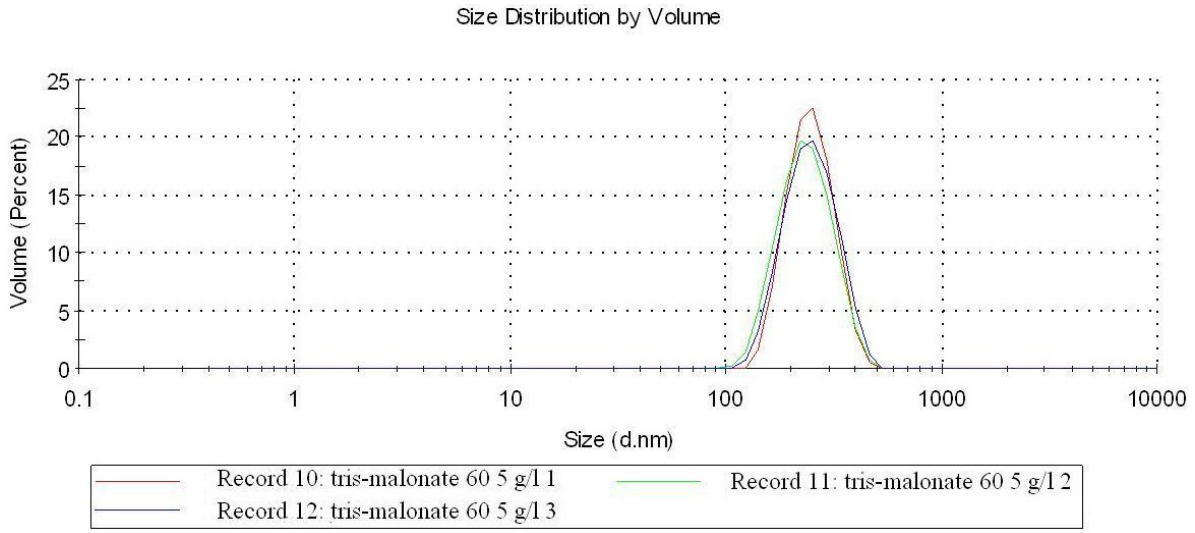

FIG. 1. Distribution according to linear dimension of C_{60} tris-malonate aggregates in aqueous solution at concentration of C_{60} tris-malonate $C = 5$ g/dm^3 (example) – 3 signals correspond to the different times of signal sum

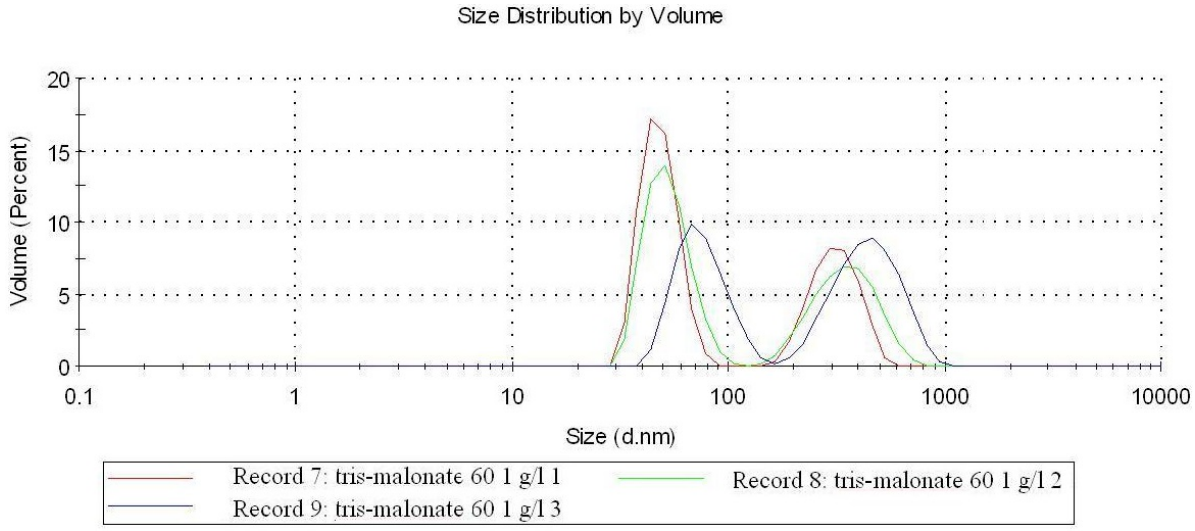

FIG. 2. Distribution according to linear dimension of C_{60} tris-malonate aggregates in aqueous solution at concentration of C_{60} tris-malonate $C = 1$ g/dm^3 (example) – 3 signals correspond to the different times of signal sum

Calculated, concerning $N_{i\to i+1}$-values data are also represented in Table 1.

From obtained data one can see the following:

1. No monomer molecular (with linear dimension-diameter $\bar{d}_0 \approx 1.8$ nm) are seen in all investigated solutions, even in the dilute solution ($C = 0.1$ g/dm^3).
2. The diameter of first type aggregates (first order clusters of percolation) have the similar linear dimension-diameter $\bar{d}_1 \approx 60 \pm 20$ nm over the whole concentration range (a slight decrease is seen only for the most dilute solution ($C = 0.01$ g/dm^3) – $\bar{d}_1 \approx 50 \pm 20$ nm).
3. The diameter of second type aggregates (second order clusters of percolation) also have a similar linear dimension-diameter $\bar{d}_2 \approx 400 \pm 100$ nm in the concentration range $0.1 \div 5$ g/dm^3 (again, a slight change is seen only for the most dilute solution at

$C = 0.01$ g/dm^3 – $\bar{d}_2 \approx 300 \pm 100$ nm and for the most concentrated solution at $C = 10$ g/dm^3 – $\bar{d}_2 \approx 750 \pm 250$ nm – solution 'is preparing to become heterogeneous').

4. Third type associates (third order clusters of percolation) have not been seen at any concentrations except the most concentrated solution at $C = 10$ g/dm^3, where clusters with extremely huge linear dimension-diameter $\bar{d}_3 \approx 5000 \pm 1000$ nm (5 ± 1 μm) are observed – the solution 'becomes very heterogeneous' but stable as a colloid system).
5. So, to describe such facts in the aggregation process, a stepwise model of particle growth was invoked. We consider that monomer spherical molecules form the first type spherical aggregates, then, the first type spherical associates form second type spherical associates. Next, the second type spherical associates form third type spherical associates (the last ones correspond to the colloidal heterogeneous system). A similar stepwise aggregation model was used by us earlier for the description of particle growth in water-fullerenol-d systems (see, for example [6]).

To prove the formation of the micro-heterogeneity (with the linear dimensions on the order of μm) in the most concentrated solution ($C = 10$ g/dm^3), we obtained a photo of the film this solution. An optical polarizing microscope Labo-Pol (variant 2) was used. Samples were prepared by the crystallization of C_{60} tris-malonate crystals from aqueous solutions under quick isothermal evaporation of water from the solution (a drop of the solution was put on the surface of silicate glass). A typical photo is represented in the Fig. 3. One can see typical spherical formations (centers of crystallization) with enough characteristic linear dimensions which were observed earlier in the dynamic light scattering investigations as third type aggregates (see Table 1). Crystal formations, proceeding from these spheres, gave the crystal-like film in the quick evaporation-crystallization process.

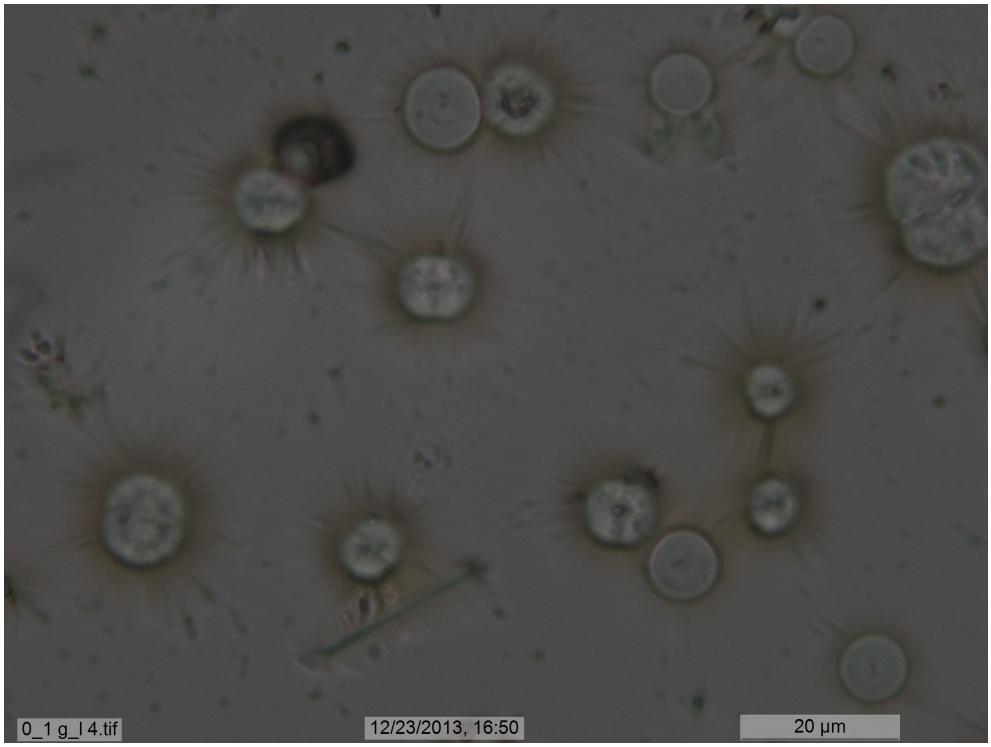

FIG. 3. Here is an optical polarizing microscope photo of C_{60} tris-malonate crystals (scale $\times 1000$). The initial (before evaporation) solution had a concentration C of 10 g C_{60} tris-malonate of per dm^3 H_2O

Acknowledgments

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References

[1] K.N.Semenov, N.A.Charykov, A.S.Kritchenkov et al. Synthesis and identification water-soluble tris-malonate of light fullerene – $C_{60}[=C(COOH)_2]_3$. *Nanosystems: Physics, Chemistry, Mathematics*, **5** (2), P. 315–319 (2014).

[2] K.N.Semenov, N.A.Charykov, A.S.Kritchenkov et al. Volume properties of water solutions and refraction at 25 °C water soluble tris-malonate of light fullerene – $C_{60}[=C(COOH)_2]_3$. *Nanosystems: Physics, Chemistry, Mathematics*, **5** (3), P. 427–434 (2014).

[3] K.N.Semenov, N.A.Charykov, A.S.Kritchenkov et al. Poly-thermal solubility and complex thermal analysis of water soluble tris-malonate of light fullerene – $C_{60}[=C(COOH)_2]_3$. *Nanosystems: Physics, Chemistry, Mathematics*. **5** (3), P. 435–440 (2014).

[4] K.N. Semenov, N.A. Charykov, A.S. Kritchenkov et al. Concentration dependence of electric conductivity and hydrogen indicator for water solutions of water soluble tris-malonate of light fullerene –$C_{60}[=C(COOH)_2]_3$. *Nanosystems: Physics, Chemistry, Mathematics*. **5** (5), P. 709–717 (2014).

[5] I. Lamparth, A. Hirsch. Water-soluble malonic acid derivatives of C_{60} with a defined three-dimensional structure. *J. Chem. Soc Chem. Commun.*, **14**, P. 1727–1728 (1994).

[6] K.N. Semenov, N.A. Charykov, V.A. Keskinov. Synthesis and Identification. Properties of Fullerenol Water Solutions. *J. Chem. Eng. Data*, **56**, P. 230–239 (2011).