



Research paper

Fractal C₆₀ fullerene aggregation: Equilibrium thermodynamics approach

Daniil A. Peidys^a, Andrei A. Mosunov^a, Yulia V. Mykhina^a, Yuriy I. Prylutsky^b,
Maxim P. Evstigneev^{a,c,*}

^a Department of Physics, Sevastopol State University, 299053 Sevastopol, Russia

^b Taras Shevchenko National University of Kyiv, Volodymyrska Str., 64, 01601 Kyiv, Ukraine

^c Laboratory of Organic Synthesis and NMR Spectroscopy, Belgorod State University, Belgorod 308015, Russian Federation

HIGHLIGHTS

- C₆₀ fullerene aggregation in solution is analyzed using EK-model.
- Equation for description DLS size distribution is derived.
- Fractal number is obtained from DLS size distribution.

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ABSTRACT

Using dynamic light scattering (DLS) data we showed that the main physico-chemical parameters characterizing C₆₀ fullerene aggregation in solution, viz. equilibrium aggregation constant and fractal number, may be obtained from equilibrium thermodynamics approach. We implemented the standard isodesmic model of aggregation for approximation of experimental particle size distribution and obtained the magnitude of fractal number, d_f , previously known from other physico-chemical methods. We propose that the suggested DLS-based approach may be applied as a method of analysis of fractal aggregation of other types of nanoparticles, such as silver, gold, or nanodiamonds, alternative to standard spectroscopic (SAXS/SANS/SLS) methods.

1. Introduction

Aggregation of C₆₀ fullerene nanoparticles in solution has attracted wide attention in the past 20 years, representing the principal physico-chemical property of these nanostructures [1–4]. Studies of aggregation have been accomplished by various physical methods and resulted in a set of general views on this process, which, in the context of the present paper, we would formulate as follows:

- C₆₀ fullerene exerts behavior of a typical colloidal nanoparticle, undergoing two limiting universal classes of aggregation kinetics, namely, a diffusion-limited aggregation (DLA, when the inter-particle energy strength is comparable with the thermal one), and reaction-limited aggregation (RLA, when the cluster growth requires a reaction-activated step), leading to irreversible coagulation [2]. Depending on the length of experiment the aggregation may either be viewed as a kinetic or quasi-equilibrium process [2,5];
- C₆₀ fullerene aqueous solution is a highly dispersed system containing fullerene aggregates (clusters) ranging by hydrodynamic

diameters from unities up to hundreds of nanometers [2,6,7];

- C₆₀ fullerene aggregation features fractal type of cluster formation, with the fractal number, d_f , ranging from 1.2 up to 2.8 [6,8,9].

Literature review suggests that quantitation of the C₆₀ fullerene aggregation has so far been studied using solely kinetic approach and the main results on quantitative parameters of aggregation were obtained only from non-equilibrium thermodynamics. However, as already discussed above, the DLA regime of aggregation suggests that within short experimental times the aggregation may be viewed as a quasi-equilibrium process governed by equilibrium thermodynamics. The key property characterizing equilibrium aggregation is the Gibbs free energy change of the reaction of aggregation, ΔG_F (and the corresponding changes in enthalpy, ΔS_F , and entropy, ΔH_F) or equilibrium aggregation constant K_F . Surprisingly, despite the very well elaborated field of small molecules reversible aggregation in solution, we were not able to find any information in literature regarding determination of ΔG_F or K_F for any type of fullerenes, except the few works, viz. the theoretical estimation of ΔG_F in [10], enthalpy/entropy change in [11]

* Corresponding author at: Department of Physics, Sevastopol State University, 299053 Sevastopol, Russia.

E-mail address: max_evstigneev@mail.ru (M.P. Evstigneev).

and the measurement of K_F in [12]. Most likely this is due to broad dispersion of fullerene clusters by dimensions, requiring per molecule enumeration from 1 up to 10^8 - 10^9 within the aggregation model [12,13], and spectral overlap [14], which provide an obstacle in numerical analysis of experimental data. In the present work we show that some key properties of C_{60} fullerene aggregation may be directly obtained from equilibrium thermodynamics approach.

2. Experimental

The pristine C_{60} fullerene aqueous colloid solutions (C_{60} FAS) used in the experiments, were prepared as follows [7,11,12]: a saturated solution of C_{60} fullerene (99.5% purity) in toluene was mixed with the same amount of distilled water and the resulted two-phase system was subjected to the ultrasonic treatment until a completion of the toluene evaporation. Afterwards, the yellow-colored water phase was filtered for removing the un-dissolved C_{60} fullerenes. C_{60} FAS was prepared in 0.1 mg/ml ($1.39 \cdot 10^{-4}$ M) C_{60} fullerene concentration in distilled water.

Preliminary characterization of the obtained C_{60} fullerene products was carried out using UV/VIS spectroscopy and atomic force microscopy (AFM) in aqueous solution. Results (not shown) agree with literature data well, indicating that C_{60} fullerene aqueous solution was formed (see [7] and references therein).

The size distribution of C_{60} fullerene aggregates was measured by dynamic light scattering (DLS) at various concentrations in the range 0.07–0.002 mM at a 99° scattering angle on a DAWN® HELEOS™ 243-HHC (Wyatt Technology Corp.) DLS instrument equipped with a Ga-As laser (60 mW) operating at a wavelength of 658.0 nm. Measurements at each concentration point were performed in triplicate and mean value was calculated.

3. Results and discussion

Fig. 1 shows the typical DLS size distribution obtained at each experimental point for the prepared C_{60} FAS, qualitatively well agreeing with literature data (see [6–8] for instance). The concentration/temperature curves have been already described before (see [11,12]), whereas the size distribution has never ever been linked to equilibrium quantities of fullerene aggregation, such as equilibrium concentrations or aggregation constant. If the fullerene aggregation follows the DLA

regime, hence, the immediate size distribution is governed by a counterbalance of colloidal forces favoring aggregate growth and thermal motion favoring aggregates' disruption. Therefore we conclude that the DLS-derived size distribution must contain information on the equilibrium quantities of aggregation, and this issue has so far been uninvestigated. Taking it as a starting hypothesis we shall further re-evaluate the size distribution of C_{60} fullerene aggregation in terms of equilibrium thermodynamics approach.

Let us assume that the C_{60} FAS is at quasi-equilibrium state, i.e. the time of observation is much longer than the diffusion timescale for C_{60} molecules ($\sim 10^{-6}$ s [15]) and much shorter than the reaction-limited timescale for C_{60} fullerene clusters ($\sim 10^6$ s [2]). In such state the equilibrium is formed by reversible binding of single C_{60} molecules, F_1 , to C_{60} fullerene clusters, F_i , containing i molecules, with equilibrium constant, K_F , according to reaction



Let us assume that the binding occurs in non-cooperative manner, i.e. K_F does not depend on the number of C_{60} molecules, i , in cluster. So, in this case we deal with K_F averaged over all i . Reaction (1) is known as isodesmic type of molecular aggregation (or self-association) and represents one of the most widely used approach in physical chemistry to study the aggregation phenomena [16]. The isodesmic aggregation (1) may be quantified by the EK-model, in which the concentration, f_i , of each cluster, F_i , is determined by mass action law [16]

$$f_i = K_F^{i-1} f_1^i = \frac{1}{K_F} a^i \quad (2)$$

where f_1 is the concentration of single (non-bound) C_{60} molecules; $a = K_F f_1$.

The total concentration of the C_{60} molecules, f_0 , is given by running over all i

$$f_0 = \sum_{i=1}^{\infty} i f_i = \frac{f_1}{(1 - K_F f_1)^2} = \frac{1}{K_F} \frac{a}{(1 - a)^2} \quad (3)$$

from which f_1 may be evaluated. Having the concentration of any cluster in solution explicitly determined as a function of K_F and f_0 , it is possible now to apply this model to description of DLS data of C_{60} fullerene aggregation.

The typical DLS experiment measures the intensity autocorrelation

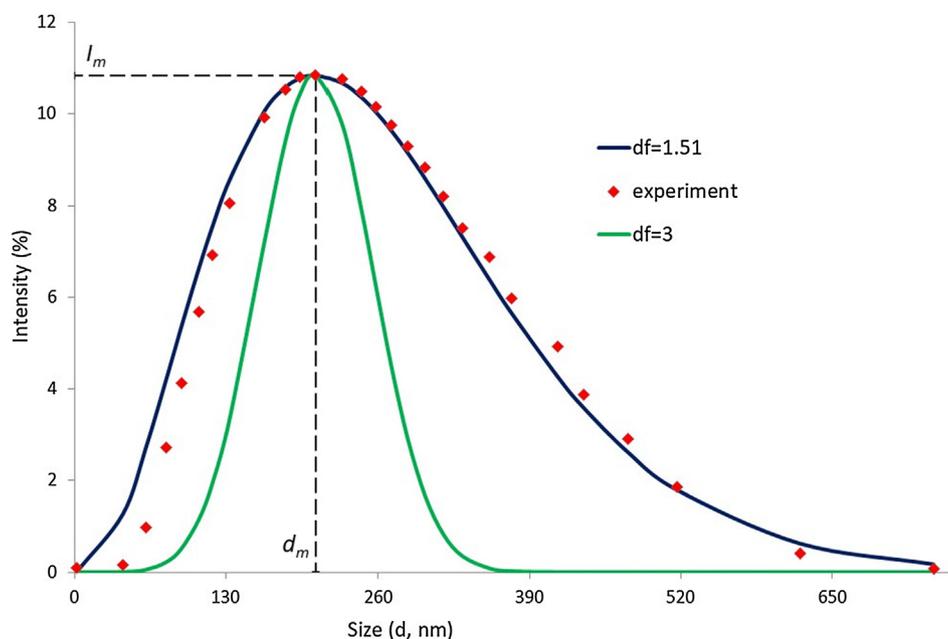


Fig. 1. DLS particle size distribution.

function, $C(\tau)$, as [17,18]

$$C(\tau) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T I(t)I(t + \tau)dt = \langle I \rangle^2 (1 + b |g_1(\tau)|^2) \quad (4)$$

where $I(t)$ is the scattered intensity (photon count rates) at some arbitrary time, t ; τ is the delay time between two counts; T is the total experiment duration over which the products of intensities are averaged; b is an experimental constant; $g_1(\tau)$ is the first-order correlation function; $\langle I \rangle^2$ is the square of the mean intensity.

For polydisperse solution of fullerene clusters the first-order correlation function is given as [17,18]

$$g_1(\tau) = \int_0^\infty G(D) \exp(-Dq^2\tau) dD \quad (5)$$

where $G(D)$ represents the relative scattering contribution of particular fullerene cluster, F_i , with the diffusion coefficient, D_i (or hydrodynamic diameter, d_i , linked with D_i through Stokes-Einstein equation); q is the wave vector. In typical DLS experiment Eq. (5) is subjected to inverse Laplace transformation yielding $G(d_i)$ as a particle size distribution, proportional to the intensity, I_i , of light scattered from a cluster containing i fullerene molecules.

Fig. 1 demonstrates the typical bell-like shape of experimental DLS particle size distribution for C_{60} molecules. The shape of the distribution is determined by competition of small scattering from large number of smaller clusters and large scattering from small number of larger clusters. For each cluster containing i particles and having molecular weight, M_i , the link to scattered intensity, I_i , is given by [19]

$$I_i \sim M_i^2 f_i P_i(\theta) C(f_i) \quad (6)$$

where $P_i(\theta)$ is the cluster form-factor and $C(f_i)$ is the concentration factor. As long as DLS experiment is performed at fixed angle, θ , and the shape of fullerene clusters is known to be mainly spherical [2,7], it is reasonable to put $P_i(\theta)$ as a constant value (this assumption will additionally be discussed below). Similar may be related to $C(f_i)$ as well, as the fullerene solution used in this work is too diluted ($f_0 \sim 10^{-4}$ M) enabling to ignore non-ideality due to cluster-cluster interaction. It thus follows that Eq. (2) substituted into Eq. (6) yields $I_i \sim M_i^2 f_i i^2 a^i$ which in definite form can be written with the proportionality constant, A , independent of the number i :

$$I_i = A \cdot i^2 \cdot a^i \quad (7)$$

Introducing further the value of maximum scattering intensity, I_m , corresponding to a cluster, d_m , one can re-evaluate Eq. (7) excluding constant A :

$$I_i = I_m \cdot \left(\frac{i}{d_m}\right)^2 \cdot a^{i-d_m} \quad (8)$$

The condition of extremum for Eq. (8) is satisfied at

$$a = e^{-2/i_m} \quad (9)$$

Now it is reasonable to replace i , d_m in Eqs. (8) and (9) by the corresponding diameters, d_i , d_m , directly measured from the particle size distribution. The most common approach used in such case is the approximation of the C_{60} fullerene clusters as spheroid objects (see, e.g. [20]), which results in standard relation

$$i = \left(\frac{d_i}{d_1}\right)^3 \quad (10)$$

where d_1 is the diameter of a single C_{60} molecule.

Substitution of Eq. (10) into Eqs. (8) and (9) yields

$$I_i = I_m \cdot \left(\frac{d_i}{d_m}\right)^6 \cdot e^{2 \left[1 - \left(\frac{d_i}{d_m}\right)^3\right]} \quad (11)$$

Distribution Eq. (11) was further used to fit experimental DLS

particle size distributions at each concentration point. Execution of this procedure evidenced very poor fit with strong underestimation of the cluster contributions (see Fig. 1 as an example at a given concentration point). We further assumed that this result may be the consequence of ignoring the cooperativity of aggregation (i.e. the dependence of K_F on i , see above). The physical nature of cooperativity for small molecules on reversible aggregate formation (not associated with chemical transformation of the reagents) may be associated with the change in the number of degrees of freedom [21], increase of the aggregate surface available for binding [15], action of colloidal repulsive-attractive potential [22]. Each of these factors can be evaluated into functional form $\Delta G_F(i)$ giving the profile $K_F(i)$ and resulting in modified Eq. (11)-like size distribution accounting for the cooperativity (not shown). However, none of these factors or their combinations led to satisfactory fitting of DLS particle size distribution in Fig. 1. It means that the cooperativity of fullerene aggregation is not the principal factor determining the particle size distribution.

It has long been known that fullerene aggregation leads to formation of clusters characterized by fractal structure displayed either as deviation from spherical shape and/or irregular packing of fullerenes inside the clusters [6,8,9]. Let us introduce the fractal property of the fullerene aggregation into the model Eq. (11) in terms of the fractal number, d_f [23,24]:

$$i \approx \left(\frac{d_i}{d_1}\right)^{d_f} \quad (12)$$

For ideal spheroid clusters with regular packing of single fullerenes $d_f = 3$ and Eq. (12) becomes identical to Eq. (10). Substitution of Eq. (12) into Eqs. (9) and (11) gives

$$a = e^{-2 \left(\frac{d_1}{d_m}\right)^{d_f}} \quad (13)$$

$$I_i = I_m \cdot \left(\frac{d_i}{d_m}\right)^{2d_f} \cdot e^{2 \left[1 - \left(\frac{d_i}{d_m}\right)^{d_f}\right]} \quad (14)$$

Fitting of experimental DLS distributions using Eq. (14) at each concentration point resulted in excellent goodness of fit equal on average to $R^2 = 0.92$ at $d_f = 1.51 \pm 0.17$ (we calculated mean value of d_f for each of $9 \times 3 = 27$ DLS distributions measured in triple for 9 concentrations). It thus may be concluded that the account for fractal dimension in the aggregation model should be considered as the most principal factor, and the use of standard approach based on Eqs. (10) and (11) is inappropriate in case of fullerene aggregation. This result is similar to the failure in description of small-angle neutron scattering (SANS) curves for C_{60} fullerene aggregates using spherical approach reported in [25]. Analysis of d_f calculated at different concentrations did not reveal any statistically meaningful change of the fractal number within the range of dispersion of experimental points (Fig. 2), suggesting that the fractal structure of the fullerene clusters remains constant. At this point it is worth noting that the obtained value of the fractal number, $d_f = 1.51 \pm 0.17$, may either be understood as a consequence of formation of non-spherical clusters, or, alternatively, spherical clusters with irregular packing of fullerenes inside them. Literature review suggests that the majority of published data which employ atomic force [7,11] or high resolution electronic [6,20,26] microscopies evidence the spherical shape of the C_{60} fullerene clusters in solution with possible deviation from sphere specifically for large clusters with diameters > 100 nm [6,9,27]. This fact provides scientific reasoning for a quite widespread utilization of spherical models in analytical description of some C_{60} fullerene properties in solution (e.g. [13,20]). It means that the spherical approach used in this work to derive Eq. (7) is physically appropriate. From the other hand, many authors agree in view that the packing of individual fullerene molecules inside the fullerene clusters is irregular. The C_{60} fullerene clusters typically contain crystal-like nucleus surrounded by amorphous shell of

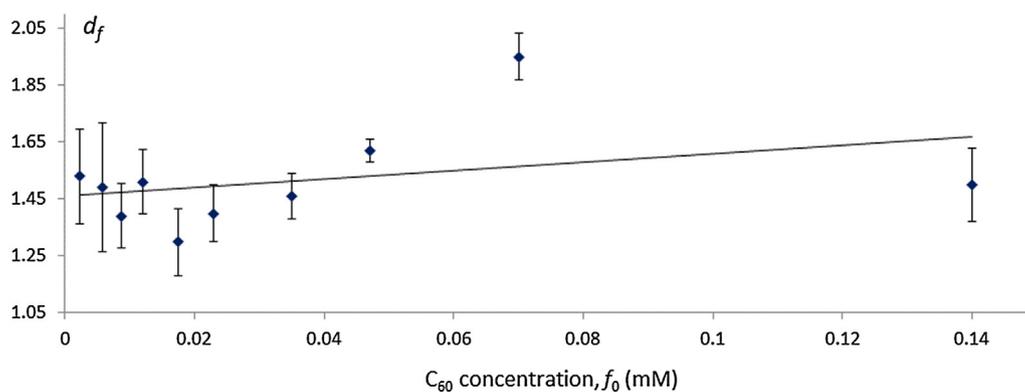


Fig. 2. Concentration dependence of fractal number.

the fullerene molecules, commonly discussed in terms of voids filled by solvent molecules [8,27,28] or formation of pores [6,9]. This packing irregularity explains the formation of fractal fullerene clusters and is responsible for the observed lowering of the fractal number, d_f .

Let us further discuss the physical appropriateness of the obtained results and usability of the suggested approach of DLS particle size distribution treatment based on Eq. (14).

Literature review evidences the very broad dispersion of d_f parameter for C_{60} fullerene clusters, ranging from 1.2 to 2.8. It indicates both highly open or porous and compact/dense structures, respectively, typically measured by static light scattering (SLS) or small-angle X-ray scattering (SAXS)/SANS [8,9]. Different authors assign the values of $d_f < 2$ specifically to the diffusion-limited aggregation regime [8,29,30], which is close to that determined in the present work. It points out on physical appropriateness of Eq. (14). Noteworthy, the functional form of the size distribution in Eq. (14) resembles that determined long time ago from the solution of Smoluchowski equations describing nanoparticles' aggregation kinetics [31]. The observed similarity is due to the fact that both the Smoluchowski equations and Eq. (14) are grounded on evaluation of mutual probability of cluster formation from smaller clusters as a product of independent probabilities of their finding in solution. This is often called 'the law of mass action', which is expressed in partial case of the EK-model in Eq. (2). In more general view, the obtained results confirm the possibility of studying the C_{60} fullerene aggregation in terms of equilibrium thermodynamics as a reversible self-aggregation process, declared before by some authors (e.g. [2,5,32]), but never implemented in experimental research.

Let us further consider the applicability of Eq. (14) and its possible benefit in practical studies of colloid aggregations. It is a common approach in such methods as SAXS/SANS/SLS to determine d_f by means of variation of the wave vector, q (see [8,9,30] for instance). However, the fundamental problem in application of these methods to fractal structure determination is the restricted range of q variation originated from limited sensitivity of each particular method. As a consequence, some authors consider that d_f determined from SAXS/SANS/SLS can only be taken as qualitative indicator of the fractal nature, but not as a quantitative measure [6] (with an aim to overcome this problem some authors even suggest to combine SAXS and SLS approach in order to cover the whole range of q variation [33]). By that reason direct comparison of d_f measured by different methods is not correct (e.g. the $d_f = 2.37$ obtained in [6] from SLS is not directly comparable with $d_f = 1.51$ measured in this work), creating a challenge for further studies. In contrast, the approach suggested in the present work is independent of q and enables determination of d_f from a single measurement of particle size distribution (with all other system parameters remained fixed) in the whole range of sizes allowed by DLS instrument ($< 10 \mu\text{m}$). To the best of our knowledge, similar result has never been reported before. We propose that for other nanoparticles, e.g. silver/gold nanoparticles, nanodiamonds, which strongly aggregate in solution and feature broad

unimodal size distributions measured in experiment, the suggested method based on Eq. (14) may also be utilized as an alternative to conventional methods such as SAXS/SANS and SLS. Another important issue is that the DLS particle size distribution, Eq. (14), was derived in this work from the knowledge of the basic mechanism of fullerene isodesmic aggregation (see Eqs. (1) and (2)). In contrast to that, the most common approach currently used elsewhere to treat DLS data is to restore particle size distribution from the measurement of the intensity autocorrelation function (Eq. (4)) by means of numerical transformation of Eq. (5) with further fitting by empirically selected functions (e.g. log normal or Schulz-Zimm functions [18]). Hence, the fitting of experimental DLS data may be accomplished by the 'physically-defined' particle size distribution as an alternative to the empirical functions. In practice, it means that Eq. (14) may be incorporated into standard software used by commercially available DLS instruments as a procedure of DLS data fitting and/or automatic d_f determination.

The equilibrium thermodynamics approach discussed above provides a new opportunity for expansion the arsenal of physical chemists for investigation the aggregation of nanoparticles. Assuming that an estimate of d_f parameter is known from independent spectroscopic study (SAXS, SANS, SLS or DLS), one can use Eq. (13) and d_m , measured from particle size distribution, to determine a . In theory, knowledge of a enables to estimate the magnitude of equilibrium aggregation constant, K_F , from Eq. (3) at single concentration point as

$$K_F = \frac{a}{f_0(1-a)^2} \quad (15)$$

However, there is a difficulty in direct application of Eq. (15) for K_F estimation for aggregation of particular nanoparticles in solution. Eq. (15) originates from application of the EK-model which explicitly defines the set of microscopic reversible reactions Eq. (1) forming dynamic equilibrium of clusters in solution. In each particular case of nanoparticles' aggregation the particular model may be different, i.e. the determination of K_F is always model-dependent. In case of C_{60} fullerene it is considered that the aggregation proceeds by formation of aggregates, which contain a compact core with diameter, d_0 , and M molecules in it, not disrupted even at infinite dilution [6,12], and having the concentration expressed in terms of fullerene monomer molecules (estimated as $C'_{M0} \approx 10^{-5}$ M at the highest fullerene concentration [12]). The aggregation is considered as simultaneous binding of R fullerene molecules at concentration, C_{R1} , with the core aggregates with macroscopic equilibrium aggregation constant, K_R . It follows, that specifically for the C_{60} fullerene aggregation Eq. (15) should be rewritten as

$$K_R = \frac{a}{C'_{M0}(1-a)^2} \quad (16)$$

where $a = K_R C_{R1}$.

The link between microscopic constant, K_F , and macroscopic constant, K_R , is given as $K_R = K_F \cdot R = K_F \cdot B \cdot M$, where $B = 0.914$,

$M = (d_0/d_1)^3$, $d_1 = 0.7$ nm, $d_0 = 280$ nm [12]. According to the data in [12] the 100-fold dilution (i.e. $C'_{M0} \approx 10^{-7}$ M at which cluster–cluster interaction may be neglected) gives $d_m \approx 280$ nm. Now, the value of K_F can be estimated as 10^6 M, which is close to that reported in [12] from dilution study. Although this result claims to be just a way to estimate the magnitude of K_F , it, in fact, evidences the internal agreement of various approaches to the description of C_{60} fullerene aggregation, used in the present work and based on equilibrium thermodynamics.

4. Conclusion

Using DLS data we showed that the main physico-chemical parameters characterizing C_{60} fullerene aggregation in aqueous solution, viz. equilibrium aggregation constant and fractal number, may be obtained from equilibrium thermodynamics approach. The key idea of the performed study is to implement the standard isodesmic model of aggregation (the EK-model) for approximation of particle size distribution measured in standard DLS experiment. Such analysis was accomplished in the present work yielding, to the best of our knowledge, the first demonstration of successful fitting of DLS particle size distribution evaluated in terms of the ‘physically-defined’ Eq. (14) derived from the aggregation model. The results evidence that the suggested approach enables determination of the value of fractal number, d_f , as well as the correct estimation of the magnitude of equilibrium aggregation constant. It confirms the possibility of application of the instruments of equilibrium thermodynamics to fullerene aggregation studies. Moreover, the developed method of d_f determination, based on single measurement of DLS particle size distribution in the whole range of particle sizes, may be superior to the application of standard spectroscopic SAXS/SANS/SLS methods (which use variation of the wave vector, q , and provide qualitative rather than quantitative estimate of d_f (due to restricted range of q variation)). It thus would be interesting to apply this method to analysis of fractal aggregation of other types of nanoparticles (such as silver, gold, or nanodiamonds). The main limitation of the suggested approach is the utilization of spherical approximation of fractal fullerene clusters, which should be additionally testified when applied to other types of nanoparticles.

CRedit authorship contribution statement

Daniil A. Peidys: Investigation, Data curation. **Andrei A. Mosunov:** Funding acquisition, Investigation. **Yulia V. Mykhina:** Visualization, Data curation. **Yuriy I. Prylutskiy:** Resources. **Maxim P. Evstigneev:** Investigation, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] D.Y. Lyon, L.K. Adams, J.C. Falkner, P.J. Alvarez, Antibacterial activity of fullerene water suspensions: effects of preparation method and particle size, *Environ. Sci. Technol.* 40 (14) (2006) 4360–4366.
- [2] N.O. Mchedlov-Petrosyan, Fullerenes in liquid media: an unsettling intrusion into the solution chemistry, *Chem. Rev.* 113 (7) (2013) 5149–5193.
- [3] A. Astefanei, O. Núñez, M.T. Galceran, Characterisation and determination of fullerenes: a critical review, *Anal. Chim. Acta* 882 (2015) 1–21.
- [4] N. Aich, L.K. Boateng, I.V. Sabaraya, D. Das, J.R. Flora, N.B. Saleh, Aggregation kinetics of higher-order fullerene clusters in aquatic systems, *Environ. Sci. Technol.* 50 (7) (2016) 3562–3571.
- [5] S. Nath, H. Pal, A.V. Sapre, J.P. Mittal, Solvatochromism, aggregation and photochemical properties of fullerenes, C~6–0 and C~7–0 solution, *J. Photosci.* 10 (1) (2003) 105–120.
- [6] J.A. Brant, J. Labille, J.Y. Bottero, M.R. Wiesner, Characterizing the impact of preparation method on fullerene cluster structure and chemistry, *Langmuir* 22 (8) (2006) 3878–3885.
- [7] U. Ritter, Y.I. Prylutskiy, M.P. Evstigneev, N.A. Davidenko, V.V. Cherepanov, A.I. Senenko, A.G. Naumovets, Structural features of highly stable reproducible C60 fullerene aqueous colloid solution probed by various techniques, *Fuller. Nanotub. Carbon Nanostruct.* 23 (6) (2015) 530–534.
- [8] Z. Meng, S.M. Hashmi, M. Elimelech, Aggregation rate and fractal dimension of fullerene nanoparticles via simultaneous multiangle static and dynamic light scattering measurement, *J. Colloid Interface Sci.* 392 (2013) 27–33.
- [9] J. Gigault, B. Grassl, Improving the understanding of fullerene (nC60) aggregate structures: fractal dimension characterization by static light scattering coupled to asymmetrical flow field flow fractionation, *J. Colloid Interface Sci.* 502 (2017) 193–200.
- [10] X. Zhao, A. Striolo, P.T. Cummings, C60 binds to and deforms nucleotides, *Biophys. J.* 89 (6) (2005) 3856–3862.
- [11] D.P. Voronin, A.S. Buchelnikov, V.V. Kostjukov, S.V. Khrapaty, D. Wyrzykowski, J. Piosik, M.P. Evstigneev, Evidence of entropically driven C60 fullerene aggregation in aqueous solution, *J. Chem. Phys.* 140 (10) (2014) 104909.
- [12] Y.I. Prylutskiy, A.S. Buchelnikov, D.P. Voronin, V.V. Kostjukov, U. Ritter, J.A. Parkinson, M.P. Evstigneev, C 60 fullerene aggregation in aqueous solution, *PCCP* 15 (23) (2013) 9351–9360.
- [13] M.V. Avdeev, V.L. Aksenov, T.V. Tropin, Models of cluster formation in solutions of fullerenes, *Russ. J. Phys. Chem. A* 84 (8) (2010) 1273–1283.
- [14] S. Nath, H. Pal, A.V. Sapre, J.P. Mittal, Solvatochromism, Aggregation and Photochemical Properties of Fullerenes, C60 and C70 solution, *J. Photosci.* 10 (1) (2003) 105–120.
- [15] V.N. Bezmelnitsyn, A.V. Eletsii, Fullerenes in solutions, *Physics-uspekhi* 41 (11) (1998) 1091.
- [16] R.B. Martin, Comparisons of indefinite self-association models, *Chem. Rev.* 96 (8) (1996) 3043–3064.
- [17] M. Filella, J. Zhang, M.E. Newman, J. Buffle, Analytical applications of photon correlation spectroscopy for size distribution measurements of natural colloidal suspensions: capabilities and limitations, *Colloids Surf. A* 120 (1997) 27–46.
- [18] J.C. Thomas, The determination of log normal particle size distributions by dynamic light scattering, *J. Colloid Interface Sci.* 117 (1) (1987) 187–192.
- [19] W. Tschamuter, Photon correlation spectroscopy in particle sizing in *Encyclopedia of analytical chemistry*, John Wiley & Sons Ltd., 2006.
- [20] R.G. Alargova, S. Deguchi, K. Tsujii, Stable colloidal dispersions of fullerenes in polar organic solvents, *J. Am. Chem. Soc.* 123 (43) (2001) 10460–10467.
- [21] M.P. Evstigneev, A.O. Lantushenko, I.V. Golovchenko, Hidden entropic contribution in the thermodynamics of molecular complexation, *PCCP* 18 (11) (2016) 7617–7625.
- [22] D.L. Van Hying, W.G. Klempner, C.F. Zukoski, Silver nanoparticle formation: predictions and verification of the aggregative growth model, *Langmuir* 17 (11) (2001) 3128–3135.
- [23] C.M. Sorensen, Light scattering by fractal aggregates: a review, *Aerosol Sci. Technol.* 35 (2) (2001) 648–687.
- [24] A.V. Eletsii, M.V. Okun, B.M. Smirnov, Growth of fractal structures in fullerene solutions, *Phys. Scr.* 55 (3) (1997) 363–366.
- [25] A.O. Khokhryakov, M.V. Avdeev, V.L. Aksenov, L.A. Bulavin, Structural organization of colloidal solution of fullerene C60 in water by data of small angle neutron scattering, *J. Mol. Liq.* 127 (1–3) (2006) 73–78.
- [26] K.L. Chen, M. Elimelech, Relating colloidal stability of fullerene (C60) nanoparticles to nanoparticle charge and electrokinetic properties, *Environ. Sci. Technol.* 43 (19) (2009) 7270–7276.
- [27] M.V. Avdeev, A.A. Khokhryakov, T.V. Tropin, G.V. Andrievsky, V.K. Klochkov, L.I. Derevyanchenko, V.L. Aksenov, Structural features of molecular-colloidal solutions of C60 fullerenes in water by small-angle neutron scattering, *Langmuir* 20 (11) (2004) 4363–4368.
- [28] K.L. Chen, M. Elimelech, Aggregation and deposition kinetics of fullerene (C60) nanoparticles, *Langmuir* 22 (26) (2006) 10994–11001.
- [29] L. Bulavin, I. Adamenko, Y. Prylutskiy, S. Durov, A. Graja, A. Bogucki, P. Scharff, Structure of fullerene C 60 in aqueous solution, *PCCP* 2 (8) (2000) 1627–1629.
- [30] M.Y. Lin, H.M. Lindsay, D.A. Weitz, R.C. Ball, R. Klein, P. Meakin, Universality in colloid aggregation, *Nature* 339 (1989) 360–362.
- [31] C. Oh, C.M. Sorensen, Light scattering study of fractal cluster aggregation near the free molecular regime, *J. Aerosol Sci.* 28 (6) (1997) 937–957.
- [32] T. Rudalevige, A.H. Francis, R. Zand, Spectroscopic studies of fullerene aggregates, *J. Phys. Chem. A* 102 (48) (1998) 9797–9802.
- [33] R.H. Guo, C.C. Hua, P.C. Lin, T.Y. Wang, S.A. Chen, Mesoscale aggregation properties of C 60 in toluene and chlorobenzene, *Soft Matter* 12 (29) (2016) 6300–6311.