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Structural coefficients in aggregates of protein-coated colloidal particles

M. Tirado-Miranda [a,*], M.A. Rodríguez-Valverde [b], A. Schmitt [a],
J. Callejas-Fernández [a], A. Fernández-Barbero [c]

[a] *Department of Applied Physics, University of Granada, Campus de Fuentenueva s/n, E-18071 Granada, Spain*
[b] *Emulsion Research Group, EUROVIA-PROBISA, E-28320 Pinto, Madrid, Spain*
[c] *Department of Applied Physics, University of Almería, E-04120 Almería, Spain*

Abstract

The structural coefficients of bare and protein-coated polystyrene particles aggregating at different electrolyte concentrations were determined by light scattering techniques. The time dependence of the average diffusion coefficient could be fitted considering a simple form for the aggregation kernel. The fits allowed the structural coefficient to be determined. This parameter was then used to obtain the surface-to-surface separation between the monomers contained within the clusters. The results show that this distance is directly related to the size of the adsorbed protein molecules.

Keywords: Structural coefficient; Cluster structure; Colloidal aggregation; Light scattering; BSA

1. Introduction

The structural and dynamical properties of colloidal aggregates play an important role in fields such as polymer and colloid science, food industries and biophysics, among others. The structure of the formed clusters is strongly related to the mechanism and kinetics of aggregation. For example, relatively open branched clusters grow under pure diffusion limited growth conditions while reaction limited aggregation processes give rise to more compact structures. Although colloidal aggregates are of very complex nature, the description of their internal structure can be significantly simplified using fractal geometry [1]. The fractal dimension, d_f, links the number of primary particles per cluster, n, to the aggregate radius of gyration, R_g, according to the relationship:

$$n = k_0 \left(\frac{R_g}{R_0}\right)^{d_f} \tag{1}$$

where R_0 is the monomer radius and k_0 is the structural coefficient. The latter parameter is often neglected and simply set to one. It is, however, an important factor for a complete quantitative characterization of fractal aggregates. In fact, clusters with identical d_f, R_g and R_0 contain less primary particles when they have a smaller structural coefficient. A larger distance should then exist among the monomeric particles contained within the clusters. Consequently, the structural coefficient k_0 must be related to that distance. Oh and Sorensen [2] expressed this dependency as $k_0 = k_0^{(1)}\delta^{d_f}$, where $\delta = 2R_0/l$ is the monomer overlap, l the center-to-center distance of two adjacent monomers and $k_0^{(1)}$ is the structural coefficient for particles that are in direct surface to surface contact. The above mentioned relationship shows clearly that k_0 increases with increasing monomer overlap. This agrees with simulations and experiments from stereoviews of three-dimensional (3D) aggregates for which high k_0 values were found [3]. The monomer overlap δ may also be expressed as:

$$\delta = \frac{2R_0}{2R_0 + S} \tag{2}$$

where S is the surface-to-surface distance of two adjacent monomers [4]. In this relationship, S is positive for separated particles and negative for overlapping monomers. In

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* Corresponding author.
E-mail address: mtirado@ugr.es (M. Tirado-Miranda).

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previous work, we studied surfactant-covered particles aggregating under diffusive conditions and the obtained S values of about twice the thickness of the adsorbed surfactant layer [4].

Information about the structural properties of aggregates can be obtained in many different ways. Scattering methods are probably the most frequently employed techniques for this purpose. They have been widely used to characterize the fractal nature of clusters and to study the underlying aggregation kinetics [5–7]. The fractal dimension of colloidal clusters is usually determined by means of static light scattering. The structural coefficient, however, is quite difficult to determine experimentally. The aggregation kinetics is normally expressed in terms of an aggregation kernel, i.e., a set of kinetic rate constants for all possible cluster–cluster reactions. Since most aggregations kernels are homogeneous functions of the cluster size, they may be classified by the well-known van Dongen–Ernst homogeneity exponent λ [8].

In this work, the structural coefficient for bare and protein-covered particles aggregating at different electrolyte conditions will be determined. The mean diffusion coefficient will be employed as experimental parameter for monitoring the aggregation kinetics. The fractal dimension of the formed aggregates and the homogeneity parameter λ will be determined by means of static light scattering (SLS) and dynamic light scattering (DLS). The results will then be used to calculate the separation between adjacent monomers contained in the clusters and to estimate the adsorbed protein layer thickness. A thorough discussion of the obtained results will show that the structural coefficient and the homogeneity exponent provide useful additional information on the cluster structure and aggregation kinetics that could not be obtained otherwise.

The paper is structured as follows: the first section is this introduction. The theoretical background is resumed briefly in Section 2. The following section details the materials and methods used for the experiments. The results are presented and discussed in Section 4. Finally, the conclusions are tackled in Section 5.

2. Theoretical background

Information on the cluster structure is frequently obtained by means of SLS. The light intensity, $I(q)$, scattered by a system with a given cluster-size distribution, N_n, is given by [6]:

$$I(q) \sim \sum_{n=1}^{\infty} N_n n^2 S(qR_g) P(qR_0) \tag{3}$$

where n is the number of monomeric particles per cluster, $S(qR_g)$ the aggregate structure factor, $P(qR_0)$ the monomer form factor, R_0 the monomer radius, R_g the aggregate radius of gyration and q is the modulus of the scattering vector. For elastic light scattering, q is given by $q \equiv (4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength of the incident beam in the surrounding medium and θ is the scattering angle with respect to the incident beam. The aggregate structure factor $S(qR_g)$ accounts for the spatial distribution of individual particles within the clusters. For $R_g \gg q^{-1} \gg R_0$, Eq. (3) may be expressed as [5]:

$$I(q) \sim (qR_g)^{-d_f} \tag{4}$$

if one assumes that the monomers are sufficiently small so that their form factor $P(qR_0)$ becomes unity. Eq. (4) allows the cluster fractal dimension to be determined directly by means of SLS measurements in the adequate q range.

The aggregation kinetics is usually studied by means of DLS. On the one hand, the electric field autocorrelation function for a polydisperse system of diffusing particles is modelled theoretical as [6]:

$$g(\tau) = \frac{1}{I(q)} \sum_{n=1}^{\infty} N_n(t) n^2 S(qR_g) P(qR_0) \exp(-\Gamma_n \tau) \tag{5}$$

where the decay rate, Γ_n, for an n-size cluster is linked to its translational, D_n, and rotational, D_n^{rot}, diffusion coefficients according to [9]:

$$\Gamma_n = D_n q^2 + 6D_n^{\mathrm{rot}} \tag{6}$$

Assuming that $D_n q^2 \gg 6D_n^{\mathrm{rot}}$ for all cluster sizes [10], the following expression may be obtained for the logarithmic derivative of $g(\tau)$ in the limit $\tau \to 0$

$$\frac{\mathrm{d}}{\mathrm{d}\tau} \ln g(\tau)|_{\tau\to 0} = \frac{-\sum_{n=1}^{\infty} N_n(t) n^2 S(qR_g) D_n q^2}{\sum_{n=1}^{\infty} N_n(t) n^2 S(qR_g)} \tag{7}$$

On the other hand, the experimentally obtained autocorrelation functions are usually fitted according to the expression [11]:

$$g(\tau) = A \exp\left(-\Gamma_a \tau + \frac{1}{2}\Gamma_b \tau^2 + \cdots\right) \tag{8}$$

which is known as cumulant analysis. Here, A is a constant, Γ_a the average decay rate and Γ_b is related to the degree of polydispersity. Evindently, the limit $\tau \to 0$ of the logarithmic derivative of $g(\tau)$ becomes:

$$\frac{\mathrm{d}}{\mathrm{d}\tau} \ln g(\tau)|_{\tau\to 0} = -\Gamma_a \tag{9}$$

Combining Eqs. (7) and (9) yields finally [6]:

$$\langle D(q,t)\rangle = \frac{\Gamma_a(q)}{q^2} = \frac{\sum_{n=1}^{n_c} N_n(t) n^2 S(qR_g) D_n}{\sum_{n=1}^{\infty} N_n(t) n^2 S(qR_g)} \tag{10}$$

where the finite character of the aggregation processes has been considered introducing a cut-off size, n_c. This cut-off size corresponds to the largest aggregates present in the system. Evidently, n_c rises as the clusters grow. Eq. (10) means that the average diffusion coefficient, obtained from experiments as $\Gamma_a(q)/q^2$, may be calculated theoretically as the average of the diffusion coefficients, D_n, of individual aggregates weighted by the corresponding scattering intensity and cluster mass distribution at any given time.