

Aggregation and Fate of Fullerene Nanoparticles in Aquatic Environments

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ABSTRACT

The initial aggregation kinetics of buckminsterfullerene C₆₀ nanoparticles are obtained through dynamic light scattering (DLS) in the presence of common monovalent and divalent electrolytes in natural aquatic systems. Aggregation experiments are conducted over ranges of NaCl and CaCl₂ electrolyte concentrations, and it is found that the aggregation behavior is consistent with the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. This study provides a better understanding of the fate and transport of fullerene when released into the natural aquatic environment.

Keywords: aggregation, dynamic light scattering, fullerene, nanoparticles

1 INTRODUCTION

Since the discovery of buckminsterfullerene C₆₀ in 1985 [1], it has drawn widespread attention due to its diverse potential applications in the fields of electronics, optical, and biomedical engineering [2-4]. Fullerene has unique chemical properties, likely to be related to its spherical cage-like molecular structure. With the development of a method for fullerene mass production, it is estimated that fullerene production can reach about 10 tons per year by 2007 [5]. As fullerene-based products are mass-produced and subsequently used by industries and consumers, it is inevitable that fullerene may end up in natural and engineered aquatic systems as pollutants. Since fullerene can be highly reactive, fullerene pollution may have environmental and ecological impacts. Moreover, studies have indicated that fullerene is toxic to microbes and fish [5, 6], raising concern about the adverse human health effects it may cause.

In aqueous solutions, hydrophobic fullerene molecules bind strongly to one another forming stable fullerene nanoparticles. Thus, it is likely that fullerene will exist in the form of nanoparticles when released into natural waters. The fate and transport of these nanoparticles are dependent on their aggregation behavior. This study investigates the early-stage aggregation kinetics of fullerene nanoparticles in the presence of monovalent (NaCl) and divalent (CaCl₂) electrolytes.

2 MATERIALS AND METHODS

Fullerene nanoparticles are synthesized by transferring fullerene C₆₀ (MER Corporation, Tucson, AZ) from toluene into water phase through sonication of fullerene/toluene/water mixture [7]. The suspension is filtered through a 0.2 micrometer filter (Fisherbrand, Fisher Scientific, Pittsburgh, PA), resulting in polydisperse spherical nanoparticles with diameters mostly ranging from 30 to 100 nm, as observed by TEM. The electrophoretic mobility of the nanoparticles at low ionic strength and unadjusted pH of 5.3 is measured with the ZetaPALS analyzer (Brookhaven Instruments Corp., Holtsville, NY), and they are found to be negatively charged.

The aggregation kinetics of the fullerene nanoparticles are obtained through dynamic light scattering (DLS) over ranges of electrolyte concentrations. The multi-detector light scattering unit (ALV-5000, Langen, Germany) was employed for the measurements at a scattering angle of 90°, and the room temperature was maintained at 23 °C. Details of this setup are described elsewhere [8, 9]. A predetermined amount of electrolyte stock solution, filtered with 0.1 μm filters (Anotop 25, Whatman, Middlesex, UK), was introduced into the vial containing the nanoparticle sample to induce aggregation, and the aggregation was followed over time periods of between 20 min and over 2 hrs.

Through DLS, the aggregation process is presented as the increase in the intensity-weighted hydrodynamic radius with time. To obtain the initial aggregation kinetics at a particular solution chemistry, the initial slope of the aggregation profile k is determined. The attachment efficiency α , otherwise known as the inverse stability ratio $1/W$, is then derived by normalizing the initial slope obtained under the studied chemical condition by the initial slope under favorable (or fast) aggregation conditions k_{fast} [8]:

$$\alpha = 1/W = \frac{k}{k_{fast}} \quad (1)$$

3 RESULTS AND DISCUSSION

The fullerene nanoparticles are aggregated over ranges of NaCl (58-362 mM) and CaCl₂ (2-22 mM) concentrations at unadjusted pH of 5.3. Figure 1 presents the attachment efficiencies as functions of NaCl and CaCl₂ concentrations. Across of the ranges of concentrations employed for both electrolytes, we observe the fast (diffusion-limited) and slow (reaction-limited) aggregation regimes. This demonstrates that DLVO-type interactions describe the aggregate behavior adequately in the presence of NaCl and CaCl₂. The critical coagulation concentrations (CCC) that demarcate the two regimes are about 120 mM NaCl and 4.8 mM CaCl₂. At electrolyte concentrations below the CCCs, an increase in the salt concentration will reduce the electrostatic energy barrier to aggregation between the negatively charged nanoparticles, thus leading to an increase in aggregation kinetics. At the CCCs (and higher salt concentrations), this energy barrier is eliminated, and the aggregation kinetics are controlled by diffusion. Interestingly, the CCC ratio of the monovalent to divalent electrolyte is calculated to be 25, which is in the same order as 64 which is theoretically predicted from the Schulze-Hardy rule [10]. This slight discrepancy is acceptable since it is difficult to pinpoint precisely the CCCs which divide the fast and slow regimes (Figure 1).

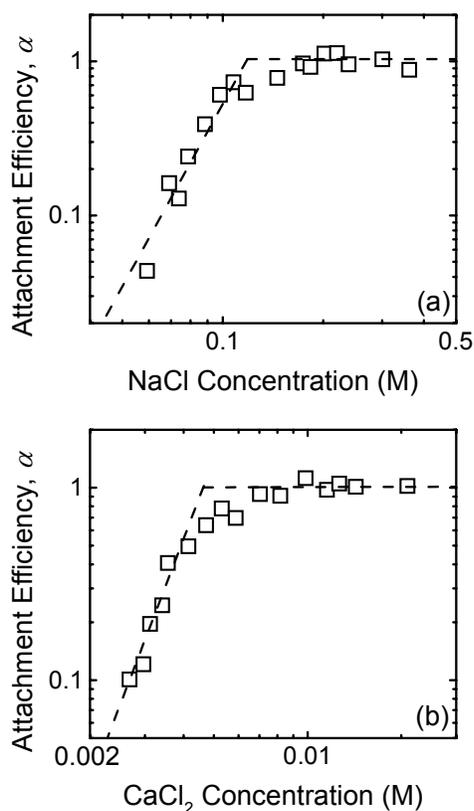


Figure 1: Attachment efficiencies as functions of (a) NaCl and (b) CaCl₂ concentrations at pH 5.3.

4 CONCLUSIONS

We have found that the aggregation behavior of the fullerene nanoparticles is similar to inorganic colloidal particles in natural waters, such as hematite and silica. The aggregation behavior can be well described by the DLVO theory. A high electrolyte concentration will destabilize the nanoparticles, leading to the formation of large aggregates. A major implication of this finding is that fullerene nanoparticles tend to remain monodisperse and suspended in aquatic systems of low salinity. This will facilitate efficient transport of the nanoparticles. In aquatic systems of high salinity, the nanoparticles aggregate readily, resulting in increased sedimentation rates and thus their removal from the aquatic phase.

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