Generation and Characterization of aqu/C_{60} aggregates in the Presence of Humic Acids

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Introduction

Many current studies on the aqueous suspension of fullerene (aqu/C_{60}) have used deionized water or simple salt solutions, and as a result little is know about the suspension of fullerene nanomatierals under environmentally relevant conditions, such as solutions that contain organic substituents and suspension exposed to sunlight. Previous reports have shown C_{60} is suspendable in the order of few to tens of mg per liter in the presence of humic acid [1, 2]. However, these reports use non-specific detection for the quantification of C60 which are prone to analyitical artifacts [3]. Additionally, the effect of humic acid concentration on the mass of C_{60} suspended and the size of aqu/C_{60} aggregates has just begun to be explored.

In this study, we report on the mass and size of aqu/C_{60} suspended in the presence of varying humic acid concentrations and upon exposure and lack of exposure to sunlight. The mass of C60 was quantified by liquid chromatography atmospheric pressure photo-ionization mass spectrometry (LC-APPI-MS). The size and size distribution of aqu/C60 were determined by dynamic light scattering (DLS) and asymmetric flow field-flow fractionation coupled to dynamic light scattering (AF4-DLS)

Experimental

Materials

Fullerene, C_{60}, (>99%) was purchased from Materials and Electrochemical Research Corp. (MER Corp., Tuscon, AZ). Suwanee river humic acid was purchased from the International humic substances society (IHSS) (Atlanta, GA). Toluene and method (HPLC grade) were purchased from Sigma-Aldrich (St. Louis, MO). Sodium Chloride (99%) was purchased from Acros (Morris Planes, NJ).

Generation of aqu/C_{60} with Humic Acid

An amount of 100 mg of C60 powder added to 400 mL of 0.1, 1.0 and 10 mg/L Suwanee River Humic Acid (SRHA), 0.45 µm filtered. Each solution was adjusted to pH 7 and 100 µS/cm ionic strength (equivalent to 1 mM NaCl). Additional,controls consisted of suspensions generated in de-ionized water. The suspensions were stirred at 200 rmps either in presence of sunlight, or in dark control experiments, wrapped in tin foil. Samples exposed to sunlight for 6 hours a day starting in late summer and samples were collected every twelve hours. Dark control samples were stirred continously and samples were collected every seven days.

Characterization by LC-APPI-MS, DLS and AF4-DLS

The Mass of C_{60} was determined liquid chromatography mass spectrometer with atmospheric pressure photo-ionization (Thermo Fisher, West Palm Beach, FL). Size and ζ porential measurements were made by dynamic light scattering in batch mode on a Malvern, Zetasizer NanoZS, Malvern (Westborough, MA) and asymmetric flow field-flow fractionation (Postnova Analytics, Salt Lake City, UT) coupled in line to the same DLS. The AF4 was outfitted with a 350 µm spacer, a 500 µL injection loop, and a 30 nm pore size polypropylene membrane, Celgard (Charlotte, NC) [5].

Results

The mass of aqu/C_{60} suspended increased over the course of 200 hours for the sunlight exposures. After 216 hours (9 days) of suspension in sunlight the concentration of C_{60} suspended in deionized water was 150 µg/L, while suspensions with SRHA had a ranged in concentration of 300 to 460 µg/L. As the mass of C60 suspened at the different SRHA concentrations was not statistically significant, the concentration of SRHA did not effect the mass of aqu/C60 suspended; however, the presence of SRHA did increase the mass suspended when compared to deionized water controls. The C_{60} concentrations reported herein are an order of magnitude less than those reported by Terashima *et al* [1] and Qilin *et al* [2] and are likely due to use of nonspecific quantification methods.

For dark controls the mass of C_{60} suspended increased over the course of 100 days. Interestingly the mass of C_{60} suspended for deionized water and various concentrations of SRHA ranged from 50 -450 µg/L. Indicating that sunlight greatly increases the rate at which C_{60} is dispersed in water, but not the concentration of aqu/C_{60}.

Batch size and ζ potential measurements by DLS of C60 suspended in SRHA solutions did not show a trend or differences between treatments for either sunlight of control experiments. However when suspensions not exposed to sunlight with 1.0 and 10 mg/L SRHA were size separated by AF4 followed by DLS, aqu/C60 ranged in size from 100-250 nm in hydrodynamic diameter (D_h) for 1 mg/L SRHA (figure 1) and 60 -110 nm in D_h for 10 mg/L SRHA (Figure 2). The observed trend of decreased aggregate size with increased SRHA results from increased steric hinderance with increased SRHA concentration. AF4-DLS measurements of of 0.1 mg/L SRHA Dark and all sunlight exposures did not scatter sufficient light to permit size determination by DLS in flow through mode, indicating that either aqu/C60 was not present in sufficient quantities or that the aggregate size was too small to allow for size determinations by DLS.

Figure 1

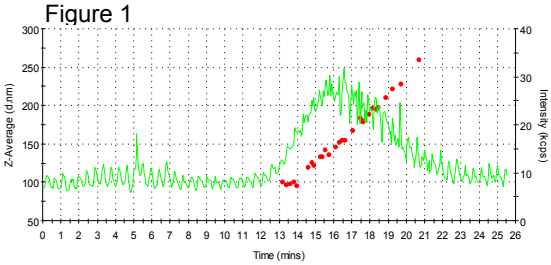
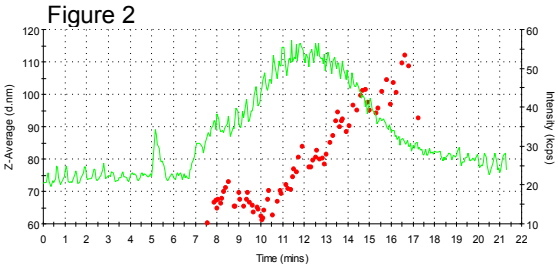


Figure 2



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