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Anion-Dependent Aggregate Formation and Charge Behavior of Colloidal Fullerenes (n-C₆₀)

Abstract

The fate and transport of colloidal fullerenes (n-C₆₀) in the environment is likely to be guided by electrostatic and aggregation behavior. In natural water bodies, organic ions exert significant effects in determining the size and charge of n-C₆₀ nanoparticles (NPs). Although the effects of cations on the behavior of n-C₆₀ NPs have been studied extensively, studies on the effect of anions are relatively few and thus were the focus of our investigation. In monovalent cation systems (Na⁺, 10 mM), Cl⁻ and SO₄²⁻ had a similar effect on the average aggregate size (D_g) and zeta potential (ζ) of suspended n-C₆₀ NPs under acidic (3.0), near neutral (5.8), and alkaline (10.0) pH conditions. Similar observations were noted in the presence of multivalent cations (Mg²⁺, 10 mM) at pH 3.0 and 5.8. However, under alkaline conditions, a strong anion-dependent reversal of surface charge was noted. The ζ changed from -65 mV, when dispersed in DI water, to +40 mV and +4 mV in the presence of Cl⁻ and SO₄²⁻, respectively at pH 10. The corresponding D_g changed simultaneously from 115 nm, in DI water, to 1450 nm and 225 nm, respectively. These findings will help explain interfacial phenomena that determine n-C₆₀ NPs transport in the environment.

Background

- Nano-scale fullerenes (C₆₀) are widely used in commercial applications^{1,2}
- Concern is growing over the impact a potential release of n-C₆₀ NPs may have on the environment
- To minimize adverse impact arising from NP exposure a critical understanding of the fate and transport of these particles in the environment is needed
- The fate and transport of n-C₆₀ NPs will largely be guided by their size and charge properties, which are functions of their surrounding environment (ionic condition, pH, etc.)³
- Inorganic ions, ubiquitous in nature, play a significant role in controlling aggregation and electrokinetic behavior of NPs
- Effects of cations (counter-ions) on the behavior of n-C₆₀ NPs are well established but investigation on the role of co-ions are rare and relatively low
- Preferential adsorption of anions (co-ions) has often been debated as a possible explanation for the acquisition of negative surface charge by n-C₆₀ NPs in aqueous media^{4,5,6}

Objective

- Compare effects of anions (co-ions) on the size and charge behaviour of suspended n-C₆₀ NPs as a function of cation (counter-ion) type and solution pH

Experimental

1. Design

Counter-ion	Cation		Fullerene	
type	mM	type	mM	n-C ₆₀ NPs (ppm) ^a
Na ⁺	10	Cl ⁻	10	-0.4
		SO ₄ ²⁻	5	
		Cl ⁻	20	
Mg ²⁺	10	SO ₄ ²⁻	10	

^a Determined using liquid chromatography atmospheric pressure photo-ionization mass spectrometry

- Each of the experiments was conducted at pH (A) 3.0, (B) 5.8 and (C) 10.0[†]
- 5.8 (near neutral) is the pH of the working standard of n-C₆₀ NP suspension in DI water
- pH was changed by adding either 5 μl of 1 (M) HCl or 1 (M) NaOH[†]
- Addition of acid or base had a negligible effect on the ionic strength of the solution

2. Procedure

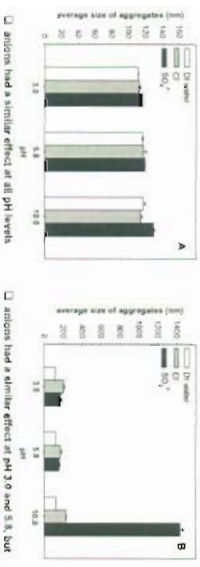
- A stock suspension of n-C₆₀ NPs was prepared by mixing ground C₆₀ in DI water by applying 10 minutes of bath sonication and filtering it through 0.45 μm filter
- 1000-μl of the stock suspension was then added to a solution of known composition to bring the final volume to 5-ml
- The resulting solution was then momentarily bath sonicated and was sampled for size and charge analysis
- The average (z-average) aggregate size (hydrodynamic diameter), D_g, and zeta potential, ζ, was measured using ZetasizerNano ZS (Malvern Instrument Inc., UK)

Experiments

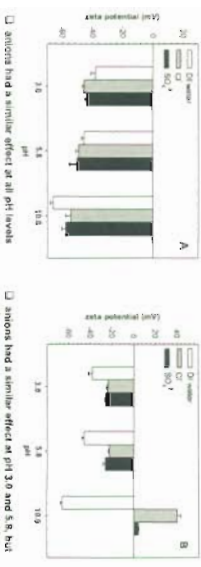
- Procedure
- For TEM analysis, samples were dropped onto 300 mesh Formvar coated copper grids and images were acquired on a Hitachi 3000 KV

Results

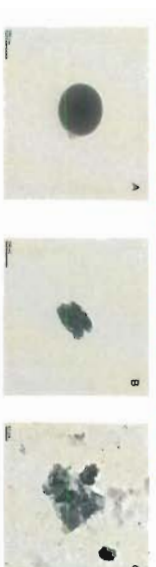
- Effect of anions on D_g as a function of (A) Na⁺ and (B) Mg²⁺ counter-ion under different pH levels



- Effect of anions on ζ as a function of (A) Na⁺ and (B) Mg²⁺ counter-ion under different pH levels



- Representative TEM of n-C₆₀ aggregates in the presence of (A) DI water, (B) 10 mM MgCl₂, and (C) 10 mM MgSO₄ at pH 10.



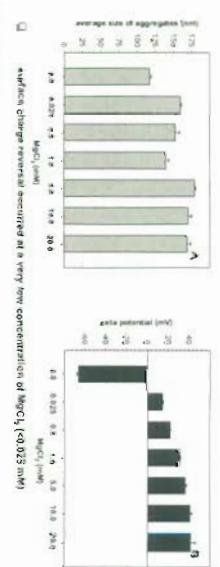
$$K = \sqrt{\frac{q^2 \sum n_i Z_i^2}{\epsilon_r \epsilon_0 k_B T}}$$

salt	mM	K ⁻¹ , nm
NaCl	3.07	
Na ₂ SO ₄	2.51	
MgCl ₂	1.77	
MgSO ₄	1.54	

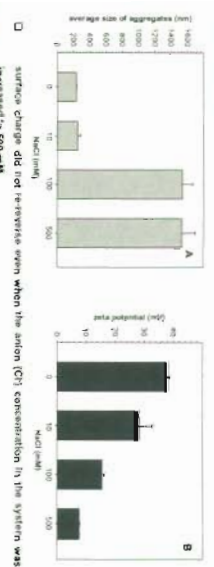
Electrostatic repulsion between particles decreases exponentially with decrease in Debye length⁷. Therefore, at a constant pH, n-C₆₀ should form larger aggregates and have lower ζ with the trend as shown by the arrow. However, this effect should be dominant at lower pH than at higher. But our results indicates not only an exception to the size but the charge behavior as well for suspended n-C₆₀ NPs.

Results

- Effect of MgCl₂ concentration of (A) D_g and (B) ζ of n-C₆₀ NPs at pH 10



- Variation of (A) D_g and (B) ζ of n-C₆₀ NPs at pH 10, with a background electrolyte concentration of 10 mM MgCl₂, as a function of NaCl concentration.



Conclusions

- When Na⁺ was the counter-ion, Cl⁻ and SO₄²⁻ had similar effects on the size and charge behaviour of suspended n-C₆₀ NPs at all pH levels
- When Mg²⁺ was the counter-ion, at pH 3.0 and 5.8, the effects of Cl⁻ and SO₄²⁻ were indistinguishable. The increase in D_g and decrease in ζ were similar, due to the presence of equal amount of Mg²⁺
- At pH 10.0, an unexpected, strong aggregation and charge reversal occurred. However, the effects were found to be function of the co-ions type: ζP changed from -65 mV in DI to +40 mV & +4 mV in the presence of Cl⁻ and SO₄²⁻, respectively
- Surface potential of n-C₆₀ NPs and charge inversion being function of pH indicated important role played by the OH⁻ co-ions. At pH 10.0, higher adsorption might cause over accumulation of Mg²⁺ resulting in charge inversion. Under this scenario, Cl⁻ and SO₄²⁻ no longer behaves as co-ion but as counter-ion. However, SO₄²⁻, because of its higher valence, cause a better screening of the positive surface charge than Cl⁻. Such an effect, was absent in monovalent systems, as the concentration development of multivalent counter-ions near surfaces can be many times higher than monovalent counter-ions.
- The above findings provide useful insight about the interfacial interactions characteristics on suspended n-C₆₀ NPs and may be utilized in drawing remediation strategies for arresting n-C₆₀ NPs transport in the environment

Acknowledgement & Disclaimer

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References

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