

Electrokinetic properties of fullerene nC₆₀ nanoparticles: Role of co-ions and pH

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Environmental exposure, bioavailability, and mobility of nanoparticles (NPs) in part depend on their aggregated state and their surface charge. These fundamental characteristics are functions of the aqueous media in which the particles are suspended. For example, inorganic ions play a significant role in determining the aggregation and electrokinetic properties of NPs. Although the role of counter-ions (ions charged oppositely to the surface charge of NPs) has been addressed by several previous studies, the literature on the role of co-ions (ions charged similarly to the surface charge of NPs) is relatively sparse. Co-ions can impact particle surface charges by preferential adsorption. This phenomenon has been debated as one possible explanation for the acquisition of negative surface charge by fullerene nC₆₀ nanoparticles (NPs) in aqueous media. In this research, a comparative study of the effects of two co-ions (SO₄²⁻ and Cl⁻) on the electrokinetic and initial aggregation behaviors of suspended nC₆₀ NPs was made under acidic (~3.0), near neutral (~6.0), and alkaline (~10.0) pH conditions. In the presence of a monovalent counter-ion (Na⁺, 10 mM), both the co-ions similarly affected the change in the average aggregate size (D_H) and the electrophoretic mobility (U_E) of nC₆₀ NPs. Similar observations were made under acidic and near neutral pH when Mg²⁺ was the counter-ion (10 mM). However, at pH 10.0, significant differences in the effects of Cl⁻ and SO₄²⁻ on D_H and U_E of nC₆₀ NPs were noted. For Cl⁻-containing treatments, U_E and D_H were 2.9 μm-cm/V-s and 250 nm, respectively. In contrast, U_E was 0.3 μm-cm/V-s and D_H was 1500 nm for SO₄²⁻-containing treatments. These compare with lower values of U_E (-4.7 μm-cm/V-s) and D_H (115 nm) for nC₆₀ in DI water at pH 10. Positive values of U_E indicate a reversal of surface charge of nC₆₀ NPs, the magnitude of which depends on the type of co-ion in the system. At, either 10 mM of MgCl₂ or MgSO₄ charge reversal occurred at pH 10.0 but not at pH 6.0 or 3.0, indicating that the starting magnitude of the surface charge in DI water played an important role in charge inversion. Although fullerene nC₆₀ is non-iogenic, the values of surface charge were proportionality related to pH. The zeta potential of nC₆₀ NPs in DI water was -70, -45, and -40 mV under the acidic, near neutral, and alkaline pH conditions, respectively. In the treatment containing 10 mM MgCl₂ as the background electrolyte, no re-reversal of surface charge was noted when the Cl⁻ concentration was increased by introducing NaCl as an

indifferent electrolyte. The measured values of U_E were 2.2, 1.2, and 0.6 $\mu\text{m-cm/V-s}$ for treatments doped additionally with 0.001, 0.1, and 0.5 M of NaCl, respectively. In addition, charge inversion for nC_{60} NPs was found to occur over a wide range of MgCl_2 concentrations, starting from as low as 2.5×10^{-5} M (U_E of 1.1 $\mu\text{m-cm/V-s}$) to a high of 2×10^{-2} M (U_E of 3.1 $\mu\text{m-cm/V-s}$), at pH 10. The effect of 10 mM CaCl_2 and 10 mM MgCl_2 were similar with respect to the aggregate size of nC_{60} NPs at pH 10; however, no charge inversion was noted in the presence of CaCl_2 unlike the case of MgCl_2 . No such differences could be established between the effects of Na^+ and K^+ with a constant Cl^- concentration of 10 mM at pH 10. All these findings indicate fundamental differences in the interfacial interaction characteristics of nC_{60} NPs with co-ions and the pivotal role played by pH (i.e., OH^-), which may allow us to better assess the behavior of nC_{60} in aquatic environments.