

# フミン酸が酸化カーボンナノホーンの凝集や帯電挙動に与える影響

## Effects of Humic Acids on Aggregation and Charging of Oxidized Carbon Nanohorn (CNHox)

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### Abstract

The effects of leonardite humic acid (LHA) on the aggregation and charging behavior of oxidized carbon nanohorn (CNHox) in aqueous solutions were experimentally studied. The electrophoretic and dynamic light scattering experiments were carried out as a function of KCl/CaCl<sub>2</sub> concentration to investigate the stability ratio and zeta potential of CNHox with/without LHA. We found the shift of critical coagulation concentration in the presence of LHA to higher electrolytes concentrations.

**Key words:** Electrophoretic mobility, Dynamic light scattering, Non-DLVO mechanisms

### 1. Introduction

Oxidized carbon nanohorn (CNHox) is one of the carbon nanomaterials and has been widely studied in industry and biomedical applications [1]. The Derjaguin-Landau and Verwey-Overbeek (DLVO) theory has been used to discuss the aggregation-dispersion of charge-stabilized colloidal particles, which is considered as an important factor to the transport behavior of nano-particles in environments. Omija *et al.* [2] have claimed that DLVO theory is applicable for CNHox with the presence of different valences of counter ions, and it has also been confirmed that highly charged counter ions had a greater effect on the surface potential of the particles than weakly charged counter ions [3]. Nevertheless, the effects of natural organic matters, which are ubiquitous in environments, on the aggregation and charging behavior of CNHox have not been extensively studied.

To obtain better insight into the effects of natural organic matters on the behavior of CNHox, we studied the zeta potential and stability ratio of CNHox in the presence of leonardite humic acid (LHA).

### 2. Materials and methods

KCl and CaCl<sub>2</sub> used in this experiment were guarantee JIS special grade, from FUJIFILM Wako Pure Chemical Corporation and dissolved in the deionized water (Elix Millipore). The CNHox used was purchased from NEC Corporation (Japan). LHA was from International Humic Substances Society.

We measured the electrophoretic mobility  $\mu$  of CNHox at different concentrations of LHA. The zeta potential  $\zeta$  was calculated from obtained electrophoretic mobility  $\mu$  using the Smoluchowski equation as:

$$\mu = \frac{\varepsilon_0 \varepsilon_r \zeta}{\eta} \quad (1)$$

$\mu$  is the electrophoretic mobility,  $\varepsilon_0$  is the permittivity of vacuum,  $\varepsilon_r$  is the relative dielectric constant of water,  $\eta$  is the viscosity of solution.

For the aggregation behavior, the dynamic light scattering method was used to get the temporal variation in average hydrodynamic diameter ( $d_h$ ) of particles by using the Stokes-Einstein equation with particles' diffusion coefficient  $D$ :

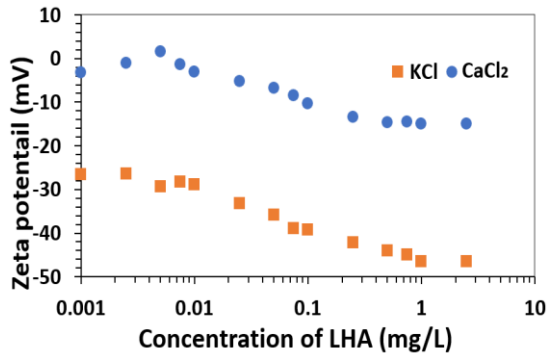
$$d_h = \frac{k_B T}{3\pi\eta D} \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\eta$  is the viscosity of solution. All the

measurements were performed as functions of electrolyte and LHA concentrations at pH between 5 and 6.

### 3. Result and discussion

Almost all the values of zeta potential of CNHox shown in **Fig. 1** are negative values and increase in magnitude with LHA concentration in two types of electrolytes, indicating the increase in the negative charge of CNHox surface due to the adsorption of negatively charged LHA. The trend of the effect of LHA in the presence of divalent cation and monovalent cation on the surface potential of CNHox is basically consistent.



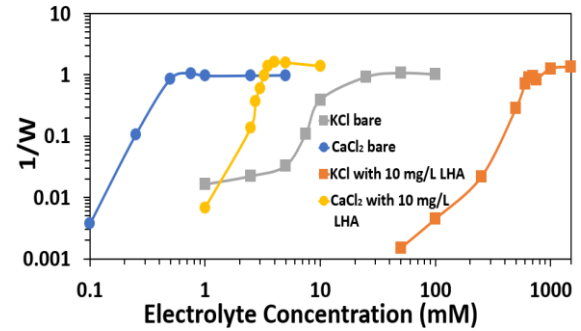
**Fig. 1** Zeta potential of CNHox as a function of the concentration of LHA and with different electrolytes at 10 mM and at pH between 5 and 6.

The stability ratio  $W$  can be converted from the aggregation rate based on the fast aggregation rate  $(dd_h/dt)^f$ , which is given by

$$W = \frac{(dd_h/dt)^f}{(dd_h/dt)} \quad (3)$$

**Fig. 2** shows the inverse stability ratio of each experiment group. The fast aggregation rate  $(dd_h/dt)^f$  used in Eq. (3) was taken from the average initial slope  $dd_h/dt$  of bare CNHox in relatively higher concentration of KCl samples. We can see the DLVO-like trend, fast aggregation regime, critical coagulation

concentration (CCC) and the shift of CCC in the presence of LHA in each electrolyte, The electrolyte concentration required for fast aggregation of CNHox becomes higher with LHA, demonstrating that LHA stabilizes the CNHox. In the case of  $\text{CaCl}_2$ , the  $1/W$  is increased in the presence of LHA after CCC compared to the bare CNHox, indicating the existence of non-DLVO mechanisms for enhancing the fast rate.



**Fig. 2** Inverse stability ratio ( $1/W$ ) of CNHox as a function of the electrolyte concentration and without or with 10 mg/L LHA at pH between 5 and 6.

### 4. Conclusion

We observed that LHA affects the surface charge of CNHox in the presence of different types of electrolytes. The aggregation of CNHox in the presence of LHA was inhibited and the shift of CCC showed qualitative agreement with DLVO theory. The non-DLVO behavior was also observed as the enhanced fast rate in high concentrations of  $\text{CaCl}_2$ .

### 5. References

- [1] M. Zhang, et al. Proceedings of the National Academy of Sciences, 105.39 (2008): 14773-14778.
- [2] K. Omija, et al. Colloids and Surface A 619 (2021): 126552
- [3] P. Sinha, et al. The Journal of Physical Chemistry Letters, 4.4 (2013): 648-652.