

Aggregation and charge reversal of humic substances in the presence of hydrophobic monovalent counter-ions: Effect of hydrophobicity of humic substances



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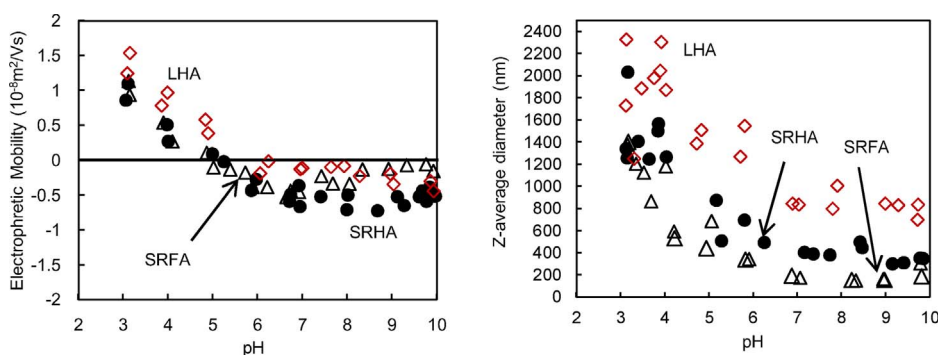
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GRAPHICAL ABSTRACT

Hydrophobicity order of three humic substances: Leonardite humic acid (LHA) > Suwannee river humic acid (SRHA) > Suwannee river fulvic acid (SRFA).



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ABSTRACT

To investigate the effect of hydrophobicity of humic substances (HSs) on their charging and aggregation, we studied the electrophoretic mobility and aggregation-dispersion of HSs in the presence of hydrophobic monovalent cations, namely, tetraphenylphosphonium TPP⁺. The used HSs were standard Suwannee river fulvic acid (SRFA), Suwannee river humic acid (SRHA), and Leonardite humic acid (LHA) with different contents of aromatic carbons. All of the HSs in the presence of TPP⁺ showed charge reversal. The charge reversal pH or isoelectric point (IEP) of LHA was higher than that of SRFA and SRHA in every concentrations of TPPCl, demonstrating the strong hydrophobic interaction between HSs, especially LHA, and TPP⁺. We also found that the formation of large visible aggregates of all the HSs at lower pH in the presence of TPP⁺. Large HS aggregates were markedly formed for LHA, manifesting the existence of stronger hydrophobic attraction among LHAs with TPP⁺. The appearance of aggregates of all the HSs with TPP⁺ was confirmed by microscopic observation and the size determination by dynamic light scattering. The HS aggregates showed fractal structure. The values of fractal dimension D_f of HS aggregates were 2–2.2 in quiescent conditions, indicating that the HS aggregates with TPP⁺ were formed via cluster-cluster aggregation with restructuring. The D_f increased to 2.8–2.9 in stirring conditions, implying that the compact aggregates were formed through the continuous aggregate breakage and the regrowth between smaller aggregates and larger aggregates.

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1. Introduction

Humic substances (HSs) are considered as one of the most important sources or sink of organic carbons in soil and water environments [1] and play a vital role in nutrient cycling, and the fate and transport of pollutants [2]. The surface active binding sites and highly reactive nature of HSs [3] influence the binding of organic and inorganic contaminants and also affect the bioavailability of metal ions and mobility in soil environment [4]. Some previous studies specially highlight on the structural heterogeneity and the molecular conformation such as supramolecular and self-assembly [5–8], fractal aggregate [9–13], and spherocolloids [14]. Some studies on the adsorption of humic substances on minerals surfaces [15] and aggregates formation [16] were carried out. The charging and aggregation behaviors of minerals particles and nanoparticles [17–20] with humic substances were also investigated. Nevertheless, there are scanty data on the structure of humic substances aggregates and the charge reversal of humic substances itself as natural colloids. A recent study on humic acid co-precipitation with ferrihydrite discussed about the unlikelihood of the humic acid used as a model colloid, though the use of humic acid as network of linear macromolecules and large colloids is more consistent [21].

Humic substances with Ca^{2+} , lysozyme, surfactants, and polymer can be aggregated to form large visible and settleable aggregates [4,22,23], which are crucially important for the fate and separation of HSs with chemicals. Generally aggregation and dispersion of colloidal particles is discussed on the basis of Derjaguin, Landau, Verwey and Overbeek (DLVO) theory, which assumes that the interparticle interaction is given as the sum of van der Waals and electrostatic interactions. The latter interaction is influenced by the electric charge of particles. The aggregation usually occurs at the condition where the net charge becomes zero. Such condition is called charge neutralization detected as an iso-electric point obtained from electrophoresis. The charge neutralization is often realized by the adsorption of appropriate amount of oppositely charged ionic substances such as polymers, surfactants, and proteins. The bindings and adsorption of metal ions depend on different factors such as pH, humic concentration, types of humic substances, ionic strength, temperature, ternary complexes formation, etc [24]. The binding of cationic surfactants to humic acid was observed due to the combined effect of electrostatic and hydrophobic interactions, whereas no notable binding was observed between anionic surfactants and humic acid [25]. In some cases the overdose of absorbable ionic substances induces charge reversal. Screening of electrostatic interaction and charge reversal are observed by the addition of various amounts of polyelectrolyte and oppositely charged ion as influenced by the amount of adsorption. Several recent researches report that the hydrophobic interaction plays an important role in charge reversal and/or charge neutralization for different natural and synthetic colloids and biomaterials [26–31].

In addition to the DLVO interaction, some other forces and interactions such as the hydrophobic interactions [22,23,26–31], hydrogen bonding [32,33], hydration forces [34,35], and depletion interactions [36] are recognized to play an important role in aggregation-dispersion of colloid particles in different environmental systems. Humic substances from different sources show the aggregation and sedimentation behaviors in the presence of inorganic salts, organic surfactants, proteins and enzymes [22,23,27,37]. Nevertheless, the mechanisms behind

the aggregation and charging behaviors of humic substances in the presence of adsorbing ions are still vague. Therefore, the research on the fundamental colloidal behavior of humic substances is still important in the field of natural colloids.

Big hydrophobic ions, such as tetraphenylboron, tetraphenylarsonium, and tetraphenylphosphonium, are used to modify the interfacial properties of clay colloids [38,39] and to monitor permeability and interaction of the lipid membranes and biological cells [40,41]. Recently, big hydrophobic tetraphenylboron anions and tetraphenylarsonium cations are also selected as tracers to study the extent of hydrophobicity of typical proteins [42]. While it is inferred that the hydrophobicity of humic substances plays crucial roles in the adsorption and aggregation, the interaction of humic substances with such big hydrophobic ions have never been reported.

In this context, we came up with performing the study on the influence of hydrophobic tetraphenylphosphonium (TPP) cations on the behaviors of humic substances. We found that TPP significantly affects the aggregation and charge reversal of three different humic substances with different hydrophobicity. In this paper, we report the result of the study on the electrophoretic mobility and aggregation behaviors of the humic substances with TPP in different concentration and pH of the solution. To the best of the authors' knowledge, our results are the first mobility data demonstrating the charge reversal of humic substances itself and thus are of novelty. We expect that the results obtained in this research can be generalized to the study of the removal of hydrophobic pollutants and aggregation-dispersion of HSs with hydrophobic organic pollutants such as dyes and drugs.

2. Experimental

2.1. Materials

Three humic substances (Suwannee river fulvic acid, Suwannee river humic acid and Leonardite humic acid) from International Humic Substances Society (IHSS) were used as natural organic matters in this study. These are referred to as SRFA, SRHA, and LHA hereafter. The primary stock solutions of the humic substances were prepared by dissolving solid samples to KOH solution (Wako Pure Chemical Industries) containing base equivalent or more than the amount of carboxylic acid groups of each humic substance. Before dissolving the solid sample to KOH solutions, the supplied samples were oven-dried at 65 °C overnight to reduce moisture. After dissolving solid humic substances to KOH solutions, the suspension (wt.%) were stirred overnight, then the secondary standard solutions were prepared by dilution with deionized water (Elix, Millipore) to a concentration 500 mg/L. The pH values of the secondary standard solutions of humic substances were around neutral (6.5–7.2). The concentration of humic substances (HSs) was maintained at 50 mg/L in every measurement in this study. Some of the parameters of the HSs from IHSS are listed in Table 1. The HSs used in this research were chosen depending on their charge groups and hydrophobicity differences based on their carbon content and aromaticity.

The electrolytes of simple KCl (JIS special grade, Wako Pure Chemical Industries) and hydrophobic tetraphenylphosphonium chloride (TPPCI) (EP grade, Tokyo Chemical Industry Co.) were used to examine the effect of hydrophobic ions. The salt concentrations were

Table 1
Some selected composition of the three humic substances reported by IHSS.

IHSS samples	Carbon content % (w/w)	Carboxylic groups (meq/g-C)	Phenolic groups (meq/g-C)	Aromatic carbon (peak area percentages) (165–110 ppm)
SRFA II (Suwannee river fulvic acid)	52.34	11.17	2.84	22
SRHA II (Suwannee river humic acid)	52.63	9.13	3.72	31
LHA (Leonardite humic acid)	63.81	7.46	2.31	58

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