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Effect of sodium oleate adsorption on the colloidal stability and zeta potential of detonation synthesized diamond particles in aqueous solutions

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Abstract

Surface properties of a nanometer-scale diamond prepared from detonation synthesis were discussed and the dispersion of this nanodiamond (ND) in aqueous solutions was actualized utilizing the method of mechanochemical treatment (MCT). While preparing a stable suspension in alkaline aqueous media, the addition of an anionic surfactant, sodium oleate (SO), can increase the absolute value of ND surface zeta potential, strengthen the electrostatic stabilization and improve the hydrophilicity of the particles. Mechanisms of the surfactant adsorption on ND surface were investigated using Fourier Transform Infrared Spectroscopy (FTIR) and the measures of particle size, surface potential and adsorption capacity of SO on particle surface. Interactions of electrostatic, hydrogen bonding, hydration, and hydrophobic have influence on the adsorption behavior of SO. Dispersion efficiency and colloidal stability behavior of ND particles are dominated markedly by the electrostatic, hydration and hydrophobic interactions among the modified particles.

Keywords: Adsorption; Colloidal stability; Diamond; Nanoparticles; Surface characterization

1. Introduction

Nanodiamond (ND, in some literature, also called ultradispersed diamond, UDD, or ultrafine diamond, UFD) investigated in this paper is a product from detonation explosion using mainly TNT, RDX, or HMX as carbonaceous precursor for diamond growth. As aggregates of ND can easily form during the process of detonation synthesis and the succeeding treatments like purification, drying, reserve and transportation; it is crucial to disperse it equably in the relevant media in order to promote its application [1–3]. Many researches on the behavior and properties of ND aggregates have been conducted in order to find a solution of stable and homogeneous dispersion [4–8]. In aqueous media, when only reagents such as surfactants or inorganic electrolytes are employed, the strength may not be strong enough to smash the so-called hard aggregates of ND particles, which are mightily bonded with each other, but while only mechanical forces are utilized, the deaggregated particles may reunite after the treatment and form coagulation again, although a phenomenon of transitory deagglomeration can be observed. Mechanochemical treatment (MCT) was introduced in our research for surface modification of ND [9]. During the mechanical treatment, the aggregates were smashed, and the simultaneous adsorption of surfactants and electrolytes on ND surface, especially on the newly created surface occurred. Through this, the stable dispersed ND suspension can be prepared.

Surfactants are employed in a variety of applications including mineral separation, detergency, and pharmaceuticals [10]. The behavior of some surfactants utilized for ND dispersion has also been discussed in some articles [6,7,11]. Sodium oleate (SO) is a surfactant widely adopted as a dispersant and collector in mineral processing. When introduced for surface modification, it exhibited good

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performance for the preparation of an alkaline stable suspension. It is a technically difficult question to actualize homogeneous dispersion of the nanosized ND particles, and there are still lots of work to carry out to make it clear the mechanism of ND deagglomeration and dispersion behavior, in this case, investigation on the effect of sodium oleate may be beneficial.

2. Materials and methods

The detonation products were usually treated firstly using hydrochloric acid to remove the metal impurities, and an atramentous product (Black powder) which contains a large content of graphite can be obtained. Further purification should be carried out to remove graphite and increase the purity of diamond products. ND-1 is a purified powder using perchloric acid to treat black powder, as for ND-2, sulfuric acid and potassium permanganate were used for graphite removing. ND-3 and ND-4 are samples after our MCT treatments with ND-1 and ND-2 as raw materials, respectively. MCT treatment can be divided to two stages, MCT1 and MCT2, while grinding technique was introduced in the former step and ultrasonic measure was adopted in MCT2.

Grain size of ND-1 and ND-2 is about 4.5–6 nm, and according to small-angle X-ray scattering (SAXS), the primary particle diameter is ranging from 1 to 60 nm with the median value of 12 nm. While it was added into aqueous media, obvious severe coagulation and sedimentation were observed and the median size was over 2000 nm. After MCT, median particle diameter in suspensions can be reduced to around 40–60 nm and all the particles are smaller than 100 nm [9].

ND-3 and ND-4 were used to study the adsorption mechanisms of SO on ND particles, while ultrasonic was used during the modification treatments. Zetasizer3000HS was utilized for size measurement of ND particles in aqueous media and for their surface zeta potential analysis. Nexus 470 was used for Fourier Transform Infrared Spectroscopy (FTIR) analysis and UV-2102 PCS was employed for adsorption analysis. Deionized water with the conductivity of less than 0.055 μs/cm was used for experiments.

3. Results and discussion

3.1. Surface properties

3.1.1. Original ND powders

Original powders, ND-1 and ND-2, were dissimilar in some characteristics as different purification techniques were used after the synthesis. Electrical surface properties of these two powders are shown in Fig.1. Curves of zeta potential versus system pH value are quite different, especially in alkaline environments.

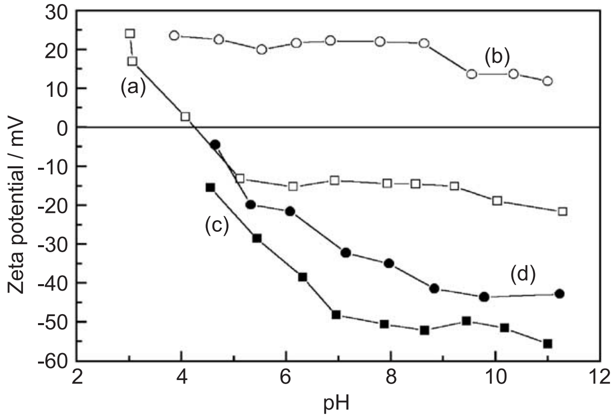

Fig. 1. Zeta potential of original ND powders in aqueous media: (a) ND-1, (b) ND-2, (c) ND-1, in 10^{-3} mol dm^{-3} SO solution, (d) ND-2, in 10^{-3} mol dm^{-3} SO solution.

As what has been analyzed in some literature [12–14], this difference may attributed to the diversity of functional groups on ND surface owing to the diversity of precursor compositions and purification measures, which can be observed by FTIR analysis, see Fig. 2. A strong and broad band of hydroxyl and amino-groups stretching vibration adsorption, with the peaks of 3433.76 and 3429.35 cm^{-1} for ND-1 and ND-2, respectively, can be observed. In addition, adsorption bands with the peaks around 2930 and 2850 cm^{-1} corresponding separately to asymmetric and symmetric stretching C–H vibration can be found in the spectra for both ND-1 and ND-2. Adsorption band with the peak of 1764.89 cm^{-1} corresponding to C=O vibration in carbonyl and carboxyl groups and that with the peak of 1629.29 cm^{-1} connected with the deformation N–H vibration and the deformation of water molecule are apparent in spectrum of ND-1, while the corresponding peaks for ND-2 are located at 1727.82 and 1632.47 cm^{-1}. However, considering the relative intensity, the carboxyl groups on ND-1 are much stronger than those on ND-2 surface.

The influence of purification on composition of surface groups is also quite pronounced, the strong and acute peak at 1124.45 cm^{-1} and peak at 623.40 cm^{-1} of ND-2 may connect with the inorganic sulfate ions, which originated from purification using sulfuric acid, and peaks at 1117.43 and 612.03 cm^{-1} of ND-1 may testify the influence of perchloric acid. (Peaks of 1117.43 and 1124.45 cm^{-1} may also connect with hydroxyl groups.)

As Fig. 2 shows, the main groups on ND-1 are hydroxyl, carbonyl, carboxyl, amino-groups, alkane hydrocarbon, perchlorate ions, and so forth. However, distinct difference for these two raw samples is that there exists little carboxyl groups on ND-2. This indicates that the oxidation effect of perchloric acid are much more stronger than that of sulfuric acid and potassium permanganate and that therefore, there are more functional groups formed after oxidation, such as carboxyl, exist on the surface of ND-1 particles.

The results of zeta potential and FTIR testified that the protonation of amino-groups in acidic media, and the

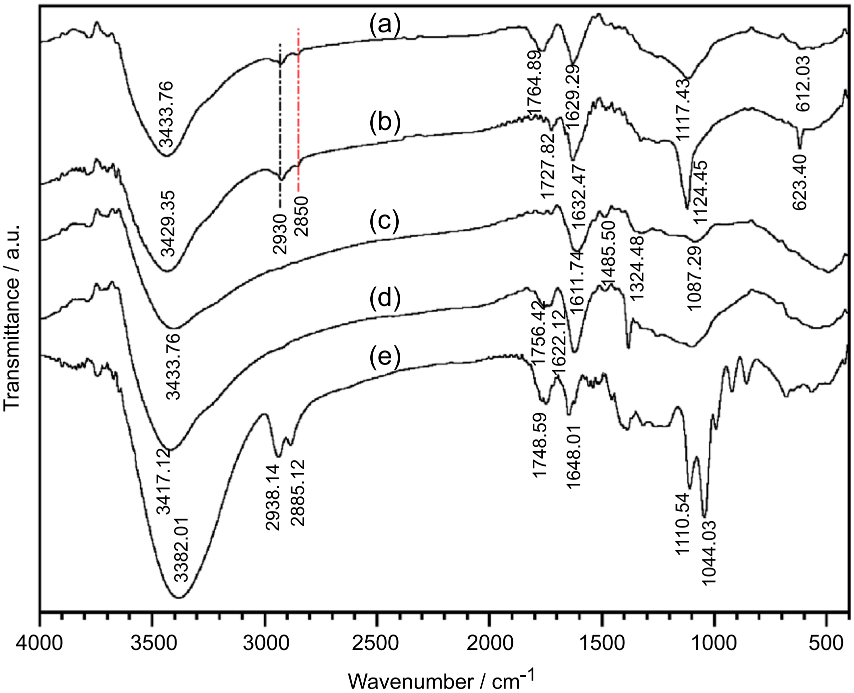

Fig. 2. FTIR spectra of original ND powders, ND during MCTs and after modification using SO: (a) ND-1, (b) ND-2, (c) ND-1, after MCT1, (d) ND-3 (namely, ND-1, after MCT2) and (e) ND-3, after modification using SO.

deprotonation of carboxyl in alkaline suspension are the main reason for the dissimilarity of surface potential (Eqs. (1) and (2)).
Acidic environment:

$$-\mathrm{NH_2} + \mathrm{H^+} \rightarrow -\mathrm{NH_3^+} \quad (1)$$

Alkaline environment:

$$-\mathrm{COOH} + \mathrm{OH^-} \rightarrow -\mathrm{COO^-} + \mathrm{H_2O} \quad (2)$$

ND-1 possesses of the both amino-groups and carboxyl on the surface, so it exhibits positive charge because of protonation effect in acidic environment, and negative charge in alkaline environment, isoelectronic point (IEP) of which located at pH 4.3 (Fig. 1). As for ND-2, as there is almost no carboxyl on it, no deprotonation effect occurred and it was positively charged in the whole pH range observed.

3.1.2. ND samples after MCT

The influence of MCT treatments on ND-1 surface functional groups can also be observed through Fig. 2. During MCT1, as drastic reactions occurred while aggregates' grinding, some cations adsorbed on ND particles and there formed carboxylate on ND surface, which can be proved by the fact that the carboxyl vibration disappeared on curve (c), and it was substitute by the asymmetric and symmetric vibration of carboxylic acid anions located at 1611.74 and 1324.48 $\mathrm{cm^{-1}}$, respectively. After MCT2, as the cations were removed from the system, and the carboxylate was decomposed, the absorption peak of carboxyl appeared again at 1756.42 $\mathrm{cm^{-1}}$.

After MCT modification, no decisive change of surface functional group type was observed, but the particle size was dramatically reduced (Fig. 3). And there is also a distinct change that the comparative intensity of carboxyl against amino-groups was decreased. Absorption band with the peaks at 1110.54 and 1044.03 $\mathrm{cm^{-1}}$ on curve (e) may attribute to the hydroxyl groups on ND surface and that of oleate molecules after the chemisorption of SO.

The contrast of zeta potential versus pH curves for ND-3 and ND-4 is similar as that between ND-1 and ND-2 despite the MCT processes (Fig. 4, when no surfactant was added). Zeta potential of ND-3 declined comparatively gentler from positive to negative than ND-1 along with the increase of pH value, and it has a higher IEP point (8.3),

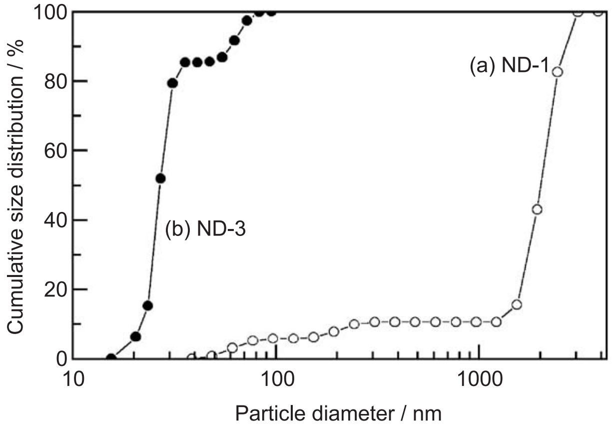

Fig. 3. Cumulative size distribution of ND in aqueous media before and after MCTs: (a) ND-1 and (b) ND-3.

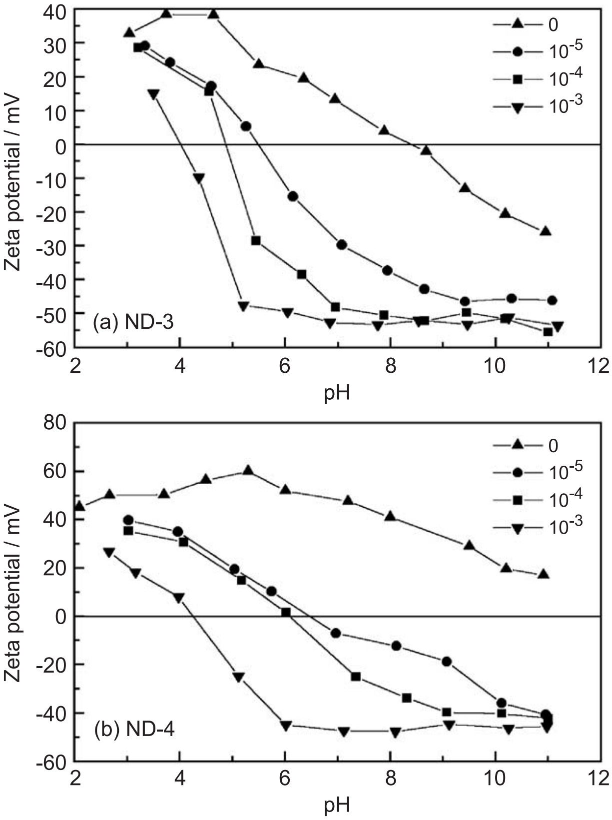

Fig. 4. Zeta potential of ND in SO solution of different concentration: (a) ND-3 and (b) ND-4.

while that of ND-4, just like ND-2, remained positive in the whole pH range. The increase of IEP of ND-3 may attribute to the increase of comparative intensity of amino-groups on particle surface which was proved by FTIR analysis above.

It is clear that, in the system prepared, the electrostatic stability plays an important role. Exhibiting high zeta potential, ND-3 and ND-4 in acidic solutions are quite stable and no aggregation and flocculation happened during a long time of observation (more than 25 months).

As the electrical surface properties are influenced in great extent by medium pH value, the electrostatic stability of ND particles are therefore affected. The relationships of average diameters of ND-3 and ND-4 particles with the system pH value are given in Fig. 5. The lower the absolute zeta potential is, the weaker the electrostatic repulsion between ND particles is, and the coarser the ND particle size would be. Around the IEP of ND-3, the particle diameter was beyond the range of Zetasizer3000HS measurements. Therefore, it is of concern to promote a further modification in alkaline environment to keep the stability of ND particles for relevant application.

3.1.3. Samples in SO solution

When ND-1 and ND-2 was added into SO solution, obvious reduction of zeta potential can be observed (Fig. 1), and the suspension are comparatively more stable than in water without SO, but the deagglomeration effect is limited.

Zeta potential of ND-3 and ND-4 in SO solutions of different concentrations were measured, see also Fig. 4, and it can be seen that the zeta–pH curves shift stepwise leftwards as the concentration of sodium oleate climbed, the lessening of zeta potential are even more obvious in alkaline environment, for both ND-3 and ND-4.

This phenomenon may originate from the adsorption of anionic surfactant, sodium oleate, on ND surface. As it was shown in FTIR analysis of ND-3 in SO solution (Fig. 2), asymmetric and symmetric stretching C–H vibration absorption bands of ND-3 were strengthened and the band of hydroxyl and amino-groups stretching vibration absorption shifted towards lower wavenumbers, these changes may be caused by the chemisorption of SO on ND-3 surface.

The status of the surfactant in the solution is crucial to the interaction between ND particles and surfactants. Protonation in acidic solution and deprotonation in alkaline solution of SO dominated its forms in the solution.

At pH 4, the main compositions of SO exist in the solution are oleic acid molecule and a little amount of dissociated oleate ions, and the zeta potential of the positively charged ND surface decrease stepwise and smoothly with the increase of SO content in the suspension (Fig. 4).

But at pH 10, see Fig.6, as SO in the system are adequately dissociated, and the oleate ions become the dominative factors on ND electrical surface properties, oleate ions adsorbed on the surface and a sharp inflexion of zeta potential can be observed with the SO concentration of around 1×10^{-5} mol dm^{-3}. For ND-3, zeta potential dropped from −15 to −50 mV, while for ND-4, zeta potential decrease sharply after the concentration of SO reached 1×10^{-5} mol dm^{-3}, the sign of zeta potential changed even from positive to negative as SO concentration climbed to about 8×10^{-5} mol dm^{-3}, and the potential decreased further to about −50 mV, like that of ND-3. Another sharp decrease of zeta potential can be measured

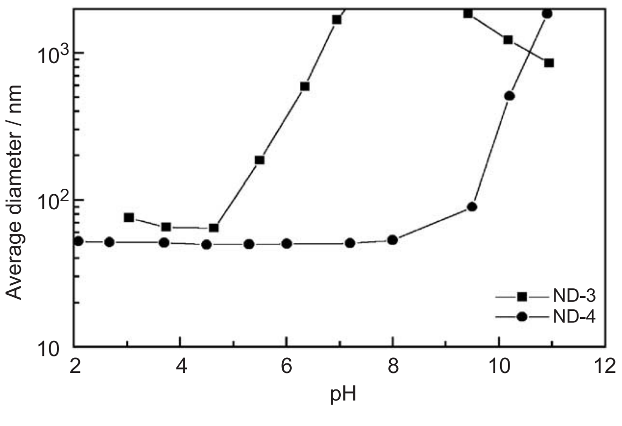

Fig. 5. Influence of suspension pH value on ND particle size after MCT.

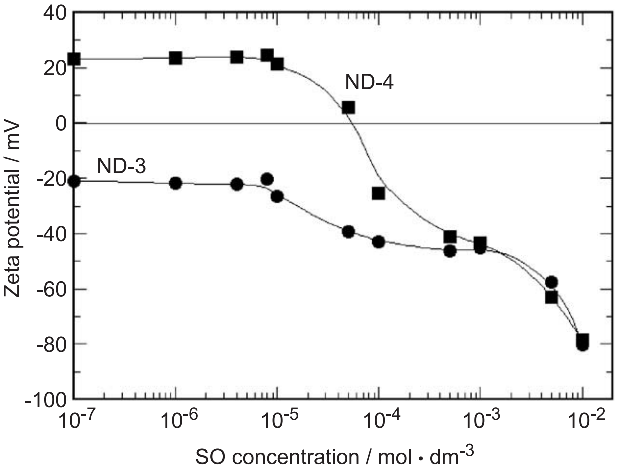

Fig. 6. Influence of SO concentration on zeta potential of ND at pH 10.

after the SO concentrate reached 1×10^{-3} mol dm^{-3}, but the data are not very credible as the poor superposition and wide distribution. This may caused by the disturbance of formation and existence of SO micelle at high concentration.

3.2. SO adsorption mechanism analysis

3.2.1. Electrostatic attraction

One of the main impetuses of SO adsorption is electrostatic attraction, that is to say, electrical surface properties of ND and the existing status of surfactants are crucial in the adsorption behavior. Figs. 4 and 6 show that, when ND stayed in an acidic solution, say, pH4, ND particles were positively charged, and the anionic ions can be attracted to particle surface easily, but the content of oleate ions was limited owing to the restricted dissociation of SO in acidic solution, therefore, only limited amount of oleate ions adsorbed on ND surface, which caused only slight reduction of positive value of zeta potential. As for ND-4, still positively charged at pH 10 has a strong tendency to attract oleate anionic ions to its surface and cause the rapid decline of zeta potential when the concentration of SO arrived at a fixed value. However, inasmuch as it is negatively charged at pH 10, ND-3 processed no obvious electrostatic attraction to oleate ions. The mechanism of ion adsorption and zeta potential decrease may be attributed to some other factors such as hydrogen bonding.

3.2.2. Hydrogen bonding

When ND surface are negatively charged, on the contrary to electrostatic attraction, an electrostatic repulsion can be observed. Despite that, oleate ion can still adsorb on the surface and even cause further reduction of zeta potential, like what occurred on ND-3 surface at pH 10, and on ND-4 too, after the zeta potential turned to be negative. The specific adsorption may attributed to the hydrogen bonding between oleate ions and some functional groups like hydroxyl or amino-groups, which can be attested through FTIR analysis, see also Fig. 2. The absorption bond of hydroxyl or amino-groups stretching vibration for ND-3 moved from 3417.12 to 3382.01 cm^{-1} after the functionalization with SO, and turned to be even more broad, this alter may caused by the hydrogen bonding effect.

3.2.3. Hydrophobic interaction of surfactants

When oleate ions were adsorbed on ND surface owing to electrostatic attraction and hydrogen bonding, nonpolar chains were exposed and extend towards aqueous media. As the nonpolar hydrocarbon chains are strongly hydrophobic, driven by hydrophobic interaction, particles with the same surface structure may unite with each other tempestuously. However, with the increase concentration of oleate ion, the hydrophobic interaction may occur between ND particle surrounded by oleate ions and the oleate ions or SO molecules in the solution, and may cause a further adsorption layer of oleate ions or SO molecules on the surface.

3.3. Schematic analysis of adsorption process

For both ND-3 and ND-4, when surface modification using SO happened in acidic solutions, as the main component is oleic acid molecule, only a small amount of oleate ions is adsorbed on ND surface and cause the slight decline of zeta potential, while the molecule forms micelle swiftly after their addition into the aqueous media and a style of O/W emulsification may occur as the solution turned to be opaque and milk white. This phenomenon can be illustrated in Fig.7(a).

At pH 10, the surface of ND-3 was negatively charged, and the adsorption of oleate ions on its surface may be

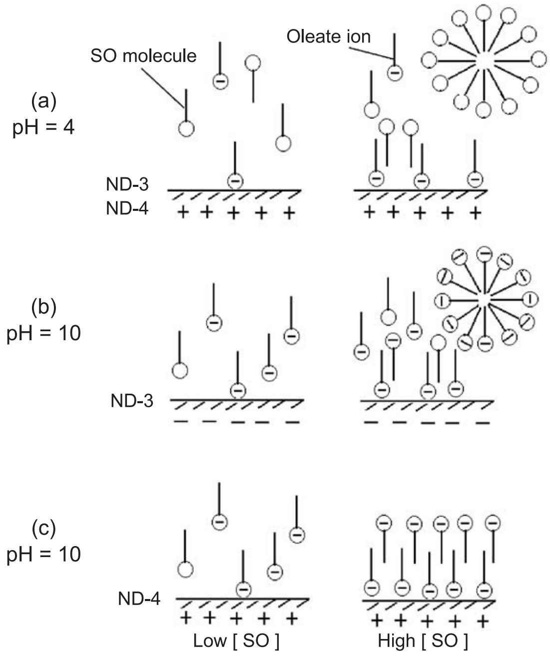

Fig. 7. Schematic illustration of SO adsorption processes (a) both ND-3 and ND-4 at pH 4, (b) ND-3 at pH 10, and (c) ND-4 at pH 10.

contributed by hydrogen bonding between polar (carboxyl) groups of SO and functional groups on ND-3 surface like amino-groups and hydroxyls. This interaction was in favor of the specific adsorption of anionic oleate ions on ND-3 surface, and caused the further reduction of zeta potential. See Fig. 7(b).

As shown in Fig 7(c), the surface of ND-4 was, on the other hand, positively charged at pH 10. Owing to the combined effect of electrostatic attraction and hydrogen bonding, oleate ions adsorbed in abundance on the surface of ND-4, and caused dramatic decline of zeta potential. During this process, ND-4 may be covered with surfactant bilayer. Ions of the first layer may bond on ND-4 using the polar ends, and with the nonpolar chains extending towards the aqueous media, because of the strong hydrophobic interaction, ND-4 particles in this surrounding can aggregate easily. However, with further addition of SO concentration, namely, after it reached at hemimecelle concentration (HMC), the second layer can form on periphery, and the nonpolar chain adsorbed on the nonpolar chain of the first layer as the hydrophobic interaction, while the hydrophilic carboxyl group pointed towards aqueous media and the hydrophilicity of ND-4 can thus be improved. This supposition was testified through the size distribution and adsorption measures of ND-4 amid the modification in the solution with the pH value of 10, see Fig. 8. The whole process can be divided roughly as four stages. At pH 10, particle was considerably coarse as the aggregation action owing to the weakened electrostatic stability (stage I); notwithstanding, it still rose rapidly with the addition of SO, especially when the concentration of SO is around 1×10^{-5} mol dm^{-3} (stage II). With the concentration climbed further, a sharp decrease of particle size was measured. Particles with average diameter of 80 nm can be obtained at the SO concentration of 3×10^{-4} mol dm^{-3} (stage III). Further increase of SO concentration shows no improving effect on size reduction; on the contrary, a slight coarsening of particle diameter was observed (stage IV).

Adsorption isotherm of SO on ND-4 surface under the same circumstances was obtained and the coincidence of four-stage-process was found. The isotherm possesses two plateaus; i.e., it is of LS-type. The SO concentration range where most severe aggregation phenomenon occurred corresponds well with the first layer of SO adsorption (the first plateau), while that where finest particles were obtained accords with the formation of bilayer adsorption.

3.4. Particle interaction during modification

According to the extended DLVO theory, energy barrier of ND particles in SO solution is determined by factors like van der Waals, electrostatic, hydration, hydrophobic, and steric interactions. Because of the coverage of surfactant layer on ND surface, the reduction of Hamaker constant, and the limited length of surfactant hydrocarbon chain, van der Waals attractive force and steric interaction for the ND-SO system are comparatively weak, the dispersion and stability behavior of ND is mainly dominated by electrostatic, hydration, and hydrophobic interactions between particles. Take ND-4 as example, with the adsorption of oleate ions, as the hydrophobic hydrocarbon chain points outwards, the hydration repulsion of particles declines rapidly, and because of the influence of hydrophobic interaction, ND particle can aggregate easily, which cause the dramatic increase of particle size (Fig. 8).

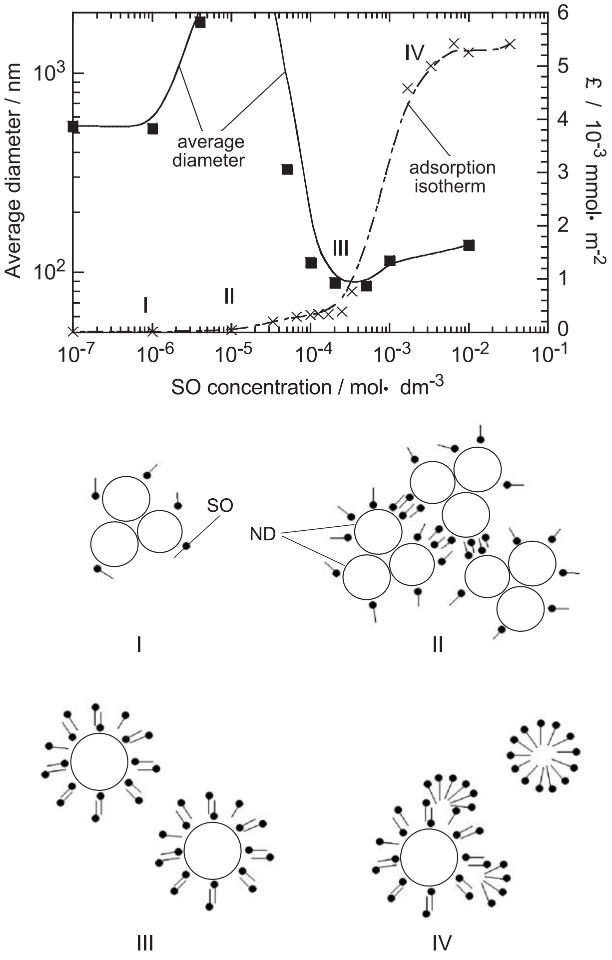

Fig. 8. Average size of ND-4 and adsorption isotherm of SO on ND-4, and schematic depiction of particle interactions of different SO concentrations (pH 10, 300 K).

After the formation of hemimicelle on ND surface, a converse phenomenon of particle size change can be observed as the polar ends of newly adsorbed surfactants strengthened the hydration effects and improved the hydrophility of ND surface; meanwhile, the hydrophobic interaction between particles was restricted.

4. Conclusions

Surface properties of ND, which finalized during synthesis and purification treatments, play an important role in the modification processes. Owing to the electrostatic interaction, the stability of ND suspensions is influenced obviously by the medium parameters, such as pH value. When introduced for ND surface modification in alkaline media, SO can increase the absolute value of ND zeta potential and strengthen the electrostatic stability; meanwhile, as the formation of bilayer SO adsorption because of hydrophobic interaction between surfactants, the polar end of SO molecules or oleate ions pointed outwards and improved the hydrophilic of particle surface. After the modification, the energy barrier of ND particle can be increased, while even distribution and stability can be realized.

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