Colloids and Surfaces A: Physicochem. Eng. Aspects 440 (2014) 202–207

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Electrokinetic properties of detonation nanodiamond aggregates in aqueous KCl solutions

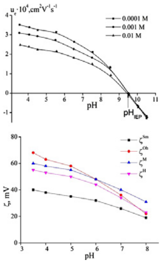
F. Gareeva[a], N. Petrova[b], O. Shenderova[c], A. Zhukov[a,*]

[a] St. Petersburg State University, St. Petersburg, Russia
[b] South Ural State University, Chelyabinsk, Russia
[c] International Technology Center, Raleigh, USA

HIGHLIGHTS

- Electrophoretic mobility of porous aggregates of detonation nanodiamond was measured.
- ζ-potential values were calculated using different equations of the theory of electrophoresis.
- Miller formula should provide the most accurate ζ-potential values for these aggregates.
- Conductivity of these porous aggregates in KCl solutions was measured.
- This conductivity is one or two orders of magnitude higher than that of solutions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 June 2012
Received in revised form 11 August 2012
Accepted 13 August 2012
Available online 2 September 2012

Keywords:
Zeta potential
Electrophoretic mobility
Detonation nanodiamond
Porous aggregates
Particle conductivity

ABSTRACT

Electrophoretic mobility of porous aggregates of detonation nanodiamond (DND) particles was measured using the laser Doppler electrophoresis technique in aqueous KCl solutions. Corresponding values of ζ-potential were calculated as functions of pH and KCl concentration using different equations of the theory of electrophoresis. It is suggested that use of the Miller formula, which takes into account the electromigration fluxes of ions and electroosmotic flows of solutions in pores of dispersed particles, should provide the most accurate ζ-potential values for DND aggregates. The hydrosols of DND purified from non-diamond carbon with nitric acid were additionally characterized by acid–base potentiometric titrations and conductometric measurements. The dependences of surface charge density and conductivity of the aggregates on the pH = 3.5–10.5 of aqueous 0.0001–0.1 M KCl solutions were obtained. The optimal values were determined for the reaction constants of ionization of acidic carboxyl (—COOH) and amphoteric hydroxyl (—COH) groups, predominant on the DND surface. It is revealed that the effective conductivity of the porous aggregates is one or two orders of magnitude higher than the conductivity of the equilibrium solutions.

1. Introduction

During the last two decades the industrial production of detonation nanodiamond (DND) powders on a commercial scale has steadily increased due to the appearance of new applications [1–4]. It is known that the detonation of a mixture of carbon-containing explosives, such as trinitrotoluene and cyclonite, in a confined space and non-oxidizing environment gives rise to the formation of nanoporous aggregates of DND ranging in sizes from tens to several hundred of nanometers and specific surface areas of 200–350 m^2/g. The aggregates consist of primary nanoparticles with a crystalline diamond lattice and very narrow size distribution in the range of

---

* Corresponding author.
E-mail address: zhuk@AZ1038.spb.edu (A. Zhukov).

0927-7757/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2012.08.055

4–5 nm. It is noteworthy that these aggregates are so strong that they cannot be broken up by high power ultrasound, but can be disaggregated into primary particles by the bead milling technique [5]. During DND processing (for example, surface functionalization) or dispersing DND in electrolytes or non-aqua media, DND aggregates can further agglomerate, like other nanoparticles [4]. It is widely accepted that the term agglomeration specifies more loosely bound particles and the term aggregation signifies very tightly bound or fused particles (typically occurring during synthesis).

It is also known that DND particles bear a variety of surface functional groups (SFGs) resulting from the processes of synthesis and subsequent liquid- or gas-phase purification from non-diamond impurities. It was established [1,2,4,7,8] that the chemical nature and densities of SFGs strongly depend on the conditions of these processes. IR and X-ray photoelectron spectroscopy [7,11–14] evidenced the presence of oxygen-containing carbonyl ($=C{=}O$), ether-like ($\equiv C{-}O{-}C\equiv$), amphoteric hydroxyl ($\equiv C{-}OH$), and acidic carboxyl ($-COOH$) groups, as well as basic amino ($\equiv C{-}NH_2$), and alkane hydrocarbon ($-CH_n$, $n = 1–3$) groups on DND surfaces. Interaction of the ionizable SFGs with aqueous electrolyte solutions leads to formation of electrical double layers (EDL) at interfaces, thus resulting in the different electrical surface phenomena observed in DND hydrosols.

An important electrosurface property of DND particles in aqueous electrolyte solutions is their electrokinetic or ζ-potential, the values of which are inherently connected with diamond surface chemistry and largely determine the colloidal stability, coagulation and rheological characteristics of DND hydrosols [6,7]. As a rule, the reported ζ-potential values of DND aggregates [6,8–11] are obtained from the electrophoretic mobility measured using laser Doppler electrophoresis and converted into ζ using Smoluchowski's classical theory of electrophoresis, which neglects the porosity and conductance of the investigated aggregates impregnated with the electrolyte solutions. It is obvious that in order to obtain the correct ζ-potential value of a given type of nanoparticle, adequate theories of electrophoresis must be applied taking into account the ranges of the applicability and validity of the underlying theoretical models.

In the current paper we report the experimental data obtained for the surface charge density and electrophoretic mobility of the various DND aggregates in the aqueous solutions 0.0001–0.01 M KCl in the range of pH = 3.5–10. Special attention is paid to identifying appropriate analytical expressions that can be used for conversion of the electrophoretic mobility's of porous DND aggregates into "actual" ζ-potential values.

2. Materials and methods

Three different DND samples that had undergone different purification methods were used in the current study. Sample 1 was a hydrosol of commercial DND purchased from "Technolog" (St. Petersburg, Russia) synthesized in an aqueous cooling medium and purified from non-diamond carbon by the treatment with 50% nitric acid at about 200 °C followed by the purification from iron impurities with hydrochloric acid and from acid impurities by dialysis. Sample 2 was a hydrosol of commercial DND powder from "New Technologies" (Chelyabinsk, Russia) synthesized in ice cooling media and purified from non-diamond carbon by treatment with a mixture of sulfuric acid with chromic anhydride. Additional purification of the sample 2 included treatment in the mixture of $NaOH/H_2O_2$, treatment by ion-exchange and fractionation down to approximately 30 nm average volumetric particle size in DI water. Sample 3 was a hydrosol of DND purified by oxidizing soot with an ozone and air mixture within the temperature interval 150–250 °C (from "New Technologies", Chelyabinsk, Russia). Since after purification the metal impurities content was high (~1.5 wt%), the sample was additionally purified with HCl and fractionated down to approximately 30 nm average volumetric particle size in DI water. As reported earlier, the average pore size for sample 3 is 8.5 nm and pores volume is 1.1 cm^3/g, as measured with the BET technique [12]. This indicates well developed porous structure of the aggregates.

The particle size distributions were determined with the dynamic light scattering technique using a Zetasizer Nano ZS (Malvern Instruments). The values of unimodal intensity-based particle effective radius R (z-average radius in Malvern's terminology) were used to estimate the parameter κR of the aggregates in electrolyte solution with a known inverse Debye length value κ.

2.1. Surface charge density

The acid–base titration of DND hydrosols (sample 1) containing 0.0001–0.1 M KCl as a background electrolyte was used to obtain the isotherms of adsorption Γ_{OH^-} (pH), Γ_{H^+} (pH) and surface charge density

$$\sigma_0(\mathrm{pH}) = F(\Gamma_{H^+} - \Gamma_{OH^-}), \tag{1}$$

where F is the Faraday constant. The titration was performed at 20–21 °C. The pH values were measured using a Seven Multi S-80-K measuring instrument (Mettler Toledo) equipped with an InLab Expert Pro pH selective combination electrode (an error of ±0.05 pH). The procedure for obtaining the adsorption isotherms is described in detail in [13].

2.2. Conductivity of DND aggregates

Conductivities K_p of DND aggregates at different pH values and KCl concentrations in hydrosols were determined from the dependences of effective conductivity K of dilute hydrosols on effective particle volume fraction ($p = 0–0.001$). The K values at the temperature 21 °C and the frequency of the imposed electric field of order 500 Hz were measured applying a Seven Multi S-80-K measuring instrument from Mettler-Toledo AG equipped with a conductometric unit and InLab 731-2m measuring electrodes (an error of ±0.005 mS/cm). The K_p values were calculated via the Street formula [14] for dilute sols ($p \ll 1$) of spherical particles

$$\frac{K}{K_v} = 1 + \frac{3}{2}p\left(\frac{K_p}{K_v} - 1\right) \tag{2}$$

and the Wagner formula [15], which takes into account the interfacial polarization

$$\frac{K}{K_v} = 1 + 3p\left(\frac{K_p - K_v}{K_p + 2K_v}\right), \tag{3}$$

where K_v is the specific conductivity of an equilibrium solution ($p = 0$).

2.3. Electrophoretic mobility of aggregates

Electrophoretic mobilities u_e of DND aggregates at an effective volume fraction $p = 0.001$ and temperature 21 °C of hydrosols containing 0.0001–0.01 M KCl at pH = 3.5–10.5 were measured using the technique of laser Doppler electrophoresis with the help of a Malvern Zetasizer Nano ZS analyzer.

2.4. Electrokinetic potential of aggregates

As a rule, ζ potentials of particles are correctly determined based on their electrophoretic mobility u_e using formulas of different electrophoresis theories [16] developed with regard to a number