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Stabilization of carbon black particles with Cetyltrimethylammoniumbromide in aqueous media

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ABSTRACT

The stabilization mechanism of aqueous carbon black suspensions by Cetyltrimethylammoniumbromide (CTAB) is studied in this paper. The adsorption of the surfactant CTAB on the carbon black particles was investigated on dried samples by thermogravimetric analyses (TGA), nitrogen adsorption and attenuated total reflection Fourier transformation infrared spectroscopy (ATR-FTIR) as well as in suspension by zeta potential measurements and atomic force microscopy. The particles are stabilized by an adsorbed CTAB monolayer as can be concluded from the results of TGA and of AFM investigations using a liquid cell. Extended DLVO calculations including the steric contribution of CTAB reveal that carbon particles with an adsorbed monolayer of CTAB exhibit sufficient colloidal stability. This result is in qualitative agreement with the experimental results.

1. Introduction

Carbon black is widely used as filler, pigment and coating additive. In the electronic industry carbon black is of importance for electrode materials in batteries and fuel cells. In the latter application carbon layers are manufactured starting from a stable dispersion of well-defined rheology. Dispersion, interparticle interactions and thus colloidal stability determine the state of aggregation, the suspension rheology, layer formation and the final structure of the films [1–15]. Therefore, the careful control of particle interactions is the key for both optimal processing and final performance of the electrode.

Particle layers have already been prepared from suspensions of several solid phases stabilized with Cetyltrimethylammoniumbromide (CTAB), e.g. zinc oxide [16], vanadium oxide composites [17], silica [18] or carbon black [19]. In preliminary investigations we found that CTAB is a suitable agent to control the interactions between carbon particles. The properties of carbon black and CTAB as well as the state of the art in describing the interactions between carbon black and CTAB are discussed below.

Carbon black is formed by partial oxidation of petroleum products in flames. Carbon black is an amorphous form of carbon with high specific surface area. The physical and chemical properties can be varied during synthesis and by post-treatment. Carbon black becomes partially crystalline by heat treatment above 2000 °C. The application properties of carbon black depend on the molecular structure of the primary particles and on the state of aggregation which can be tailored by varying the time-temperature history of the particles in the flame. By heat treatment, the surface of carbon black as well as the size and the structure of the primary particles can be modified [20]. The application of carbon black as aqueous dispersion requires careful control of particle interactions and especially of colloidal stability.

In water the cationic surfactant CTAB forms several structures depending on the concentration and pH-value. At concentrations higher than cmc micelles are formed which are spherical at pH < 4 and become wormlike at pH-values > 7 [21]. At high CTAB concentrations networks are formed. The degree of dissociation of the head groups depends on the temperature. At ambient temperature about 25% of the bromide ions are separated from the ammonium group [22].

The interaction between CTAB and carbon black in water was already studied in 1967 by Abram et al. who used CTAB adsorption as an indicator for the determination of the free surface area [23]. At a concentration of 1 mM (cmc) a plateau in the adsorbed CTAB-amount was found and further studies showed a monolayer of the surfactant on the carbon black [23]. Based on the results of atomic force microscopy Manne et al. suggest the formation of hemimicelles on graphite templated by a first flat layer of CTAB molecules. The experimentally observed orientation of the adsorbed molecules parallel to the carbon surface in water (0.8 mM CTAB solution) is explained by an interaction to the moderately conducting substrate which screens the charged head groups [24]. Half-cylindrical aggregates (half of rodlike micelles) of alkylammonium salts were also observed by Kiraly and Findenegg in 1998 for CTAB and for trialkylammonium salts with another alkyl chain length—C_{12}TAB. They put forward the reorientation model where the partial desorption of two adsorbed molecules offers space for three guest molecules. Alternatively, they described a well-ordered monolayer in the lower concentration region that serves as template for the further adsorption of molecules at higher concentrations. The

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lower layer is oriented head-to-head and tail-to-tail and the molecules situated above this layer align their ammonium groups to the water phase [25]. Bele et al. additionally took the water molecules into account and their interpretation of IR-spectra includes that the signal of one water molecule which is bound to a bromide ion differs from the signal of the bulk water [26]. He postulated a strong binding between the CTAB molecule lying flat on the surface and carbon black (cationic pi-interactions and hydrophobic effect between the carbon black and the alkyl chain of CTAB) and weak interactions between solvent and substrate (see Ref. [22]). In the case of graphitized carbon black the heat treatment influences the surface properties. For example, the formation of positively charged sulfur species leading to positive surface charges is possible. Organic sulfur compounds are formed during the synthesis of carbon black from petroleum which contains thiophene. The negative zeta potential of carbon black at pH of 10 (IEP = 6.5) changes after the adsorption of CTA^+ to positive values indicating that CTA^+ enters the electrical double layer [19].

CTAB adsorption mechanisms on silica were studied in the literature in great detail [27]. In contrast to the hydrophobic carbon black hydroxylated silica has a hydrophilic surface and therefore the CTAB molecules in the first adsorbed layer are oriented with their hydrophilic head groups to the silica surface.

As for carbon black also for silica different adsorbed CTAB layer structures have been observed: The formation of hemimicelles as an intermediate between a monolayer at low concentration and micelles at concentrations above cmc were described in a two-step model [28]. Transitions between globular micelles, cylindrical micelles and flat films were observed, but also CTAB double layers were observed which are so far not described on carbon black above cmc [18,29,30]. For a very similar molecule (C_{14}TAB) Sakai found by AFM hexagonal lattice structures instead of cylindrical micelle-like aggregation on mica and postulated small aggregates (dimers) in the solution that are adsorbing to the surface [31].

Patrick studied the effect of small variations of the stabilizing molecule (head group size, alkyl chain length) on the colloidal stability of mica. With increasing length of the alkyl chain the repulsive forces between two adjacent molecules become weaker and longer alkyl chains of the whole molecule changed the structure of adsorbed micelles from spheres (C_{12}) to short rods (C_{14}) and finally to meandering cylinders (C_{16}). These observations led to the introduction of a packing parameter as an estimation of the surfactant structure [32].

Although many studies have been published with several adsorption mechanisms of CTAB on carbon black and mica there are still fundamental questions not answered up to now: it was still not possible to distinguish between micelles, hemimicelles or bilayers [33]—especially if only a few measuring methods were chosen to characterize the adsorbed layer. According to Kiraly the adsorption of the anionic, SDS, and cationic, CTAB, surfactants on graphite follow the same mechanism – formation of monolayers at low concentrations and half-cylindrical hemimicelles above the cmc [34] – an argument, which is in conflict to the cationic pi-interactions postulated by Bele. Independent of the different properties of the several carbon black powders and the variation of the stabilizer, the interaction of the ionic head group with polar surface sites is generally accepted. Changes in the conformation of the stabilizer layer structure in dependency of the stabilizer concentration are accepted as well [35–38].

The literature survey discussed above shows that the structure and therefore the thickness of the adsorbed CTAB layer depends on the CTAB concentration and on the surface properties of the carbon used as substrate material. The adsorbed layer thickness governs the steric contribution to the total particle interaction potential and therefore the colloidal stability. Consequences regarding colloidal stability and achievable particle sizes by dispersing processes, however, are not discussed in the papers dealing with the structure of the adsorbed CTAB layer on carbon although this is important from the practical point of view.

In this paper we investigate the dispersion of carbon black in water to almost primary particle size using a stirred media mill. The cationic surfactant CTAB is used as a stabilizing agent. The dispersing experiments are combined with investigations of the mechanism of particle stabilization against agglomeration by studying the adsorbed CTAB layer. The mechanistic studies are done using different complementary methods allowing the investigation of the structure of the adsorbed CTAB layer on carbon black on dried samples (TGA, ATR-FTIR spectroscopy) and in aqueous environment (zeta potential measurements, particle size analyses and AFM measurements in a liquid cell). The AFM investigations enable studying the layer formation of the adsorbed phase by force–distance measurements and height profiles of the adsorbed layers. The results allow insights into the structure of the adsorbed CTAB layers which strongly influence colloidal stability. These results are supported by numerical estimations of the interaction potentials between CTAB coated carbon black particles. From the data presented in this paper it can be concluded that a CTAB monolayer is formed where the polar head groups protrude into the aqueous phase.

2. Experimental

2.1. Materials

Graphitized carbon black was supplied by SolviCore GmbH & Co. KG, Germany. CTAB, supplied by Carl Roth GmbH & Co. KG, Germany, with a purity of >98%, was dissolved in deionized and filtered water. As plane graphitic surface, necessary for AFM, highly ordered pyrolytic graphite (HOPG) was purchased from SPI Supplies, USA, with grade 1 (similar to grade ZYA). Before measuring fresh surfaces were created by the cleaving method.

For the calibration of the electroacoustic device for zeta potential measurements a “silica ludox” standard dispersion from Quantachrome GmbH & Co. KG, Germany, with 10 wt.% of 28 nm particles in an aqueous medium with pH 9.3 is used. The ludox suspension has a zeta potential of −38 mV ± 1 mV.

2.2. Preparation of aqueous carbon black dispersions using a stirred media mill

Aqueous dispersions of 5 wt.% graphitized carbon black with CTAB amounts between 30 wt.% and 150 wt.% (referring to the weight of carbon black) were milled for 3 h in a vertical stirred media mill “PE075” (Erich NETZSCH GmbH & Co. Holding KG, Germany) operating in the batch mode. 1.7 kg of yttria stabilized zirconia beads with a diameter of 0.8 mm were used as grinding media. During dispersion the temperature of 15 °C was kept constant and the stirrer tip speed was set to 2.8 m/s. In preliminary dispersion studies these machine parameters were found to be optimal for obtaining submicron carbon dispersions. The particle size was measured as a function of milling time by laser diffraction using a Mastersizer 2000 (Malvern Instruments GmbH, Germany). After the milling the carbon dispersion was separated from the grinding media by a sieve. At optimal CTAB concentration the mean particle diameter was about 100 nm as measured with laser diffraction, dynamic light scattering (for both methods diluted dispersions were used) and with ultrasound attenuation using the original dispersion.

2.3. Characterization of the dispersions

Electroacoustic spectroscopy (DT-1200 from Dispersion Technology, Inc., USA) at a frequency of 3 MHz was used to measure the zeta-potential. First, the instrument was calibrated using a 10 wt.% silica ludox dispersion and then the stabilized carbon black dispersions were measured in original concentration (5 wt.% carbon black).

Thermogravimetric analysis (TGA Q 50 from TA Instruments, USA) was performed in a platinum pan under nitrogen atmosphere. The