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Combined effect of cetyltrimethylammonium bromide and laponite platelets on colloidal stability of carbon nanotubes in aqueous suspensions

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ABSTRACT

The combined effect of cationic surfactant (cetyltrimethylammonium bromide, CTAB) and laponite platelets (laponite RD) on the stability of aqueous suspension of carbon nanotubes (NTs) has been investigated. The experimental methods include measurements of electrokinetic potential, radius of particles and aggregation stability. In individual suspensions the concentration of NTs was $C_n = 0.003\%$ and concentration of laponite was $C_l = 0.5\%$ and 2%. In hybrid NT + laponite suspensions the concentration of NTs was $C_n = 0.003\%$ and 0.01% and the laponite/NT mass ratio, $X = m_l/m_n$, was varied within the range of $X = 0$–1. For individual NTs and laponite species the increase of the CTAB concentration, C_s, changed the electrokinetic potential from negative to positive. However, the different effects of CTAB on stability of this species were observed: addition of CTAB stabilized the individual NTs and enhanced aggregation of laponite. The CTAB-induced overcharging was also typical for hybrid NT + laponite suspensions. Surprisingly, the minimum of a position of an isoelectric point C_s(IEP) ($\approx 3 \cdot 10^{-6}$ M) at $X \approx 0.1$–0.3 was observed. This behavior can reflect the impact of CTAB on adhesion interactions between NTs and laponite platelets and adsorption of CTAB on individual NT and laponite species and their hybrids.

1. Introduction

Carbon nanotubes (NTs) possess high tendency to aggregate in different solvents due to strong van der Waals attractive forces between individual NTs [1–4]. Moreover, in aqueous systems NTs exhibit especially low aggregation stability due to hydrophobic interactions and strong van der Waals attractive forces between individual NTs. Poor dispersability and formation of bundles or large aggregates presents a serious obstacle to good functionality of materials on the base of NTs in a number of branches of modern technology (sensors/biosensors, composite materials, catalyst supporters). Colloidal stability of aqueous suspensions of NTs can be significantly enhanced using addition of surfactants [5], charged nanoparticles (e.g., laponite platelets [6–9]) and water soluble polymers [10].

For example, cationic surfactant cetyltrimethylammonium bromide (CTAB) is widely used for stabilization of NTs in aqueous suspensions. Mechanisms of stabilization of NTs by CTAB have been mainly studied using transmission electron microscopy and Raman-scattering, measurements of adsorption and zeta potential, ζ, of NTs in wide range of CTAB concentrations including the critical micelle concentration (CMC) ($C_s^{CMC} \approx 1$ mM or 0.0364 wt% (hereinafter %) [11–14]. Multilayer adsorption of CTAB on NTs has been observed [13]. For 0.01% aqueous suspension of NTs and pH 7 the saturation level of adsorption was reached at CTAB concentration of $C_s \approx 0.9$ mM and this concentration was indicated as optimum for stabilization. CTAB facilitates the dispersion of NTs. The electrical conductivity of films obtained from NT suspensions evaporation was as high as for “pure” NTs [12] Adsorption of CTAB molecules can recharge NTs in aqueous suspensions, and the zeta potential changes from negative to positive values with an increase of C_s [13,14]. For example, for 0.175% aqueous suspension of NTs the position of the isoelectric point (IEP) was about $C_s \approx 1$ mM at pH 6.3 and the zeta potential reached saturation level of about 50 mV for $C_s \geq 2$ mM [14]. Also it has been shown that pH of medium greatly affected the zeta potential: for $C_s = 2$ mM it was ≈6.4 mV at pH 3 and ≈2.2 mV at pH 11 [14]. The stabilization of NT suspensions is controlled by CTAB concentration in aqueous suspension and the NTs-to-CTAB ratio [12]. The ζ-potential increased as the concentration of NTs, C_n, decreased and as the C_s increased. For example, at NT concentrations of $C_n = 10^{-3}\%$

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(low), 10^{-2}% (intermediate) and $2.5 \cdot 10^{-2}$% (high) and at $C_s = 0.27$ mM (below CMC), the positive ζ-potential values were 46, 30, and 25 mV, respectively and at $C_s = 2.7$ mM (above CMC), the positive ζ-potential values reached 66, 49, and 40 mV, respectively. For low concentration of NTs, $C_n = 10^{-3}$%, effective stabilization over a 15-day period was observed at CTAB concentration of $C_s = 0.27$ mM, i.e. below CMC and at $C_s = 2.7$ mM, i.e. above CMC. For higher concentration of NTs, $C_n = 2.5 \cdot 10^{-2}$%, the stabilization was more efficient at $C_s = 0.27$ mM as compared to that at $C_s = 2.7$ mM. The observed phenomena were explained by differences in adsorption of individual CTAB molecules and worm-like CTAB micelles on the NT surface. The different orientations of CTAB molecules onto NT surface have been discussed [13]. At concentrations below CMC individual molecules of CTAB interact with NTs due to electrostatic and/or hydrophobic forces and are oriented as a "flat" molecules (whole hydrocarbon skeleton lies on the NT surfaces) and only charged part of the CTAB is bound with NT (the other part of the molecule creates an oppositely charged shell around NTs).

Dispersability of NTs in aqueous suspensions can also be noticeably enhanced by obtaining pickering emulsion of NTs with laponite platelets. The effect of laponite platelets on the stabilization of carbon nanotubes suspension [6,7] and its aggregation kinetics under continuous stirring the system has been investigated [8,9]. Addition of laponite in amount of higher than 50% mass fraction of NTs produces stable aqueous suspensions (not settling within few months). The hybrid NTs + laponite particles can be coagulated by addition of salts or base/acid [8]. It has been also shown that an increase of pH increases the surface charge density and, as a result, an increase in the repulsive forces between the hybrid particles and decrease of the degree of their aggregation. Note that the size and the shape of hybrid NTs + laponite particles are determined by NTs while their adsorption properties are determined by laponite particles attached to the surface of nanotubes. Due to the presence of laponite on the sorbent surface, its adsorbing capacity was much higher as compared to the adsorbing capacity of pure NTs [7]. This sorbent may be used either as a purifying additive or as a filtering layer if it is deposited on the surface of a supporting membrane [15]. Due to relatively large size of hybrid particles, they can be easily separated from the purified solution by filtration or centrifugation that is promising for practical applications.

The combined effect of surfactant and pickering particles represents great interest and can be recommended as a new tool for stabilization of NTs in aqueous suspension. Attraction of positively charged CTAB molecules to the negatively charged faces of laponite can significantly modify the properties of pickering platelets. Adsorption of CTAB on the laponite increases the hydrophobicity of platelets and decreases the sedimentation stability of laponite suspensions [16]. This results in separation of the suspension into supernatant and flocs. At concentration of CTAB $C_s = 0.0164$% (which comprises 0.03 of the laponite cation exchange capacity, CEC) noticeable changes in the aging dynamics of the supernatant part were registered. Addition of CTAB to the laponite suspension also enhances the aging and accelerates the gelation processes. Depending on the CTAB concentration, three sedimentation regimes in laponite suspensions have been revealed: continuous ($C_s < 0.14$%), zone-like ($0.14\% < C_s < 0.2\%$) and gel-like ($C_s > 0.2$%) [16]. CTAB adsorbs on the faces of laponite platelets in an amount which exceeds the CEC value four times [17]. CTAB + laponite complex retains disk morphology even at the excess of CTAB (higher then CEC value), and its thickness turned to be higher (4 nm) compared to "pure" laponite (1 nm). Note, that laponite suppresses the formation of CTAB micelles in its solution [17]. At the same time, the combined effect of CTAB and laponite platelets on the stabilization of NT aqueous suspension has never been studied before.

The objective of this paper was to elucidate the mechanism of stabilization of NTs in aqueous suspension by mixtures of cationic CTAB surfactant and laponite nanoparticles of different composition. To solve this task, a detailed study of the electrokinetic potential and aggregation processes in individual NT and laponite aqueous suspensions in the presence of CTAB and combined effects of CTAB and laponite on the stabilization of NTs in aqueous suspension has been performed.

2. Materials and methods

2.1. Materials

The multi-walled carbon nanotubes (NTs) were produced by chemical vapour deposition method in the presence of Fe-Mo-Al catalyst (Specmash, Kyiv, Ukraine) [18]. The NTs were purified by annealing to separate from the catalyst and mineral impurities, and treated by aqueous solutions of alkali (NaOH) and hydrochloric acid (HCl). The samples were filtered to remove the excess acid and repeatedly washed by distilled water until the constant pH value of distilled water was reached. The NTs are composed of concentric shells with inter-shell distance equal to 0.34 nm, their typical outer diameter was 10–20 nm, while their length was 5–10 μm. The specific surface area of NTs, S_n, determined by nitrogen adsorption, was 254 m^2/g. The NTs have several walls within the range of ≈6–8 layers and their density varies from 1.6 g/cm^3 to ≈1.0 g/cm^3 with increasing the outer diameter from 10 nm to 20 nm [19]. According to FTIR spectra, the NT surface contained a small amount of hydroxyl and carboxylic groups and at neutral pH value their electrokinetic potential was ≈ -32 mV [19].

Laponite RD $Na_{+0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]_{-0.7}$ (Rockwood Additives Ltd., UK) is composed of charged disk-like sheets with thickness of about 1 nm and average diameter of about 25–30 nm [20]. According to literature data, its specific surface area, S_l, determined by nitrogen adsorption measurements, is 370 m^2/g [21], and its density is ≈2.53 g/cm^3 [22]. Laponite can be represented as a sheet of the six octahedral magnesium ions sandwiched between two layers of four tetrahedral silicon atoms. The laponite platelets are charged highly heterogeneously in aqueous suspensions: their faces have constant negative charge, while the surface charge of their edges is pH-dependent and it is positive in acidic medium. According to the manufacturer [22], the edge of laponite particle is positively charged below pH of 11 (see also [23] for discussion). The negative surface charge per unit weight of laponite RD, defined as its cation exchange capacity, is $CEC_l \approx 0.75$ meq/g.

NTs, laponite and hybrid NT + laponite suspensions were prepared by addition of the appropriate amounts of nanoparticles to distilled water and subsequent sonication of mixtures using the ultrasonic lab homogenizer (Heilscher GmbH, Germany) at frequency of 24 kHz and output power of 400 W. The total sonication time was 5 min. To prevent suspensions from overheating, they were sonicated in a cold-water bath, and the temperature of suspension never exceeded 40 °C. In individual suspensions the concentration of NTs was $C_n = 0.003$% and concentration of laponite was $C_l = 0.5$% and 2%. In hybrid NT + laponite suspensions the concentration of NTs was $C_n = 0.003$% and 0.01% and the laponite/NT mass ratio, $X = m_l/m_n$, was varied within the range of $X = 0$–1.

No special adjustment of pH of suspensions was performed. For NT aqueous suspensions the natural pH was ≈6.0. The pH of the suspensions increased with an increase of laponite concentration. For example, the pH values 6.5, 8.5, 9.7 and 10.0 at $C_l = 0.05$, 0.5, 1.0, and 2.0 wt%, were observed, correspondingly [16,19].

Cetyltrimethylammonium bromide (CTAB) $C_{16}H_{33}N(CH_3)_3Br$ (Fluka, Germany, 99.5%) has molar mass of $M_{s.} = 364.45$ g/mol, length of the molecule of 2.33 nm, and critical micelle concentration (CMC) in water of ≈1 mM (0.0364%) [11].

It is known that at small pH < 10 the laponite particles can undergo chemical degradation, caused by CO2, dissolved in the sample [23–25]. In order to prevent such effects all experiments were performed within 10 min immediately after preparation of suspensions.

2.2. Methods

Electrophoretic measurements were performed by ZetaSizer NS (Malvern, UK) device. The electrophoretic mobility, μ, was determined