ELECTROKINETIC STUDY OF IMPACT OF LAPONITE PLATELETS ON STABILIZATION OF CARBON NANOTUBES IN AQUEOUS SUSPENSIONS

MARYNA MANILO¹–NIKOLAI LEBOVKA²–SÁNDOR BÁRÁNY³

To characterize the electric double layers of multi-walled carbon nanotubes, laponite platelets and their hybrid particles, the electrophoretic potential was measured as a function of pH and concentration of electrolytes (KCl, CaCl₂ and AlCl₃). Nanoparticles under study have negative zeta potential value in the whole studied pH interval (2–12). An increase in pH from 2 to 12 resulted in substantial increase of the absolute (negative) values of the zeta potential of nanotubes due to dissociation of surface hydroxyl and carbonyl groups, which was identified by infra-red spectroscopy. The observed attraction between similarly charged carbon nanotubes and laponite particles was explained by highly heterogeneous distribution of negatively charged functional groups on the surface of nanotubes and difference in zeta potential of nanotubes and laponite particles.

Keywords: carbon nanotubes, laponite platelets, zeta potential, aggregation, pH, electrolytes

Introduction

Carbon nanotubes (CNTs) are promising materials for preparation of CNT-laden nanofluids [1], carbon-based catalysts [2], adsorbents for waste water treatment [3], highly selective nano- [4] and biosensors [5] and many other attractive materials with extraordinary mechanical, thermal and optical properties. Numerous applications of CNTs require their good dispersability in the media and stability of the properties. The problem is that CNTs show high tendency to aggregation due to strong van der Waals interactions in the most of solvents [6]. High hydrophobicity of CNTs may be also an important factor of aggregation in water and hydrophilic solvents [7].

Dispersability of CNTs in aqueous suspensions can be enhanced by surface treatment (for example, oxidation [8]), adsorption of polymers or surfactants and addition of other types of nanoparticles [9]. Aggregation behaviour of CNTs in the presence of surfactants [10], polymers or electrolytes [11] and at different pH values of the system [12] was studied. Addition of electrolytes to the suspension (e.g. with Na⁺, K⁺, Ca²⁺counterions) results in suppressing the electrostatic repulsion between individual CNTs and inducing their aggregation [11]. The aggregation kinetics of CNTs at different pH values, the effect of concentration of electrolytes and humic acid (HA) was evaluated [12]. The presence of HA enhanced the stability of CNTs, that was dependent on the type of electrolyte added. Similar effects were observed for CNTs with sodium dodecylbenzene sulfonate as a dispersing agent [11]. The correlations between electrokinetic potential of multi-walled CNTs, dispersability in different solvents (water, ethanol and hexane), stability of CNT suspensions, surface energy, and oxygen content of CNTs, modified by functionalization,
were discussed [13]. It was speculated that CNT dispersability in a liquid is affected by the hydrophilic character of a considerable part of the CNT surface, which is reflected by the electrokinetic potential value. Recently, the electrokinetic behaviour of multi-walled CNTs and oxidized multi-walled N-doped CNTs was also studied [14]. The electrokinetic behaviour of CNTs was similar to that observed for inorganic colloid particles. A correlation between sedimentation stability and electrosurface properties of CNTs was observed [14].

Recently, it was shown that addition of charged laponite clay platelets significantly improved the dispersability of CNTs in aqueous suspensions [9] and prevented their aggregation. However, the nature of interactions between CNTs and laponite platelets is still unclear. The important contribution may be associated with surface/electrosurface properties of CNTs, i.e., chemical nature and concentration of surface functional groups that determine wetting, surface charge density and electrokinetic potential, as well as dispersability of the nanotubes.

The aim of our paper was to elucidate the nature and mechanism of stabilization of CNT suspensions by laponite platelets and aggregation kinetics of CNTs, laponite and hybrid CNT+laponite nanoparticles in the presence of acid/base and different electrolytes. Also the zeta potential of multi-walled CNTs, laponite and hybrid CNT+laponite nanoparticles as a function of pH and electrolyte concentration was characterized.

1. Experimental Materials and Procedure

Multi-walled carbon nanotubes (CNTs) were produced by CVD method in the presence of Fe-Mo-Al catalyst (Specmash, Kyiv, Ukraine) and purified as described in [15]. CNTs 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 CNTs, determined by nitrogen adsorption, was 254 m²/g. CNTs have several walls within the range of ≈ 6–8 layers and their density varies from 1.6 g/cm³ to ≈ 1.0 g/cm³ with increasing the outer diameter from 10 nm to 20 nm [15].

Laponite RD, i.e. RD grade laponite (Rockwood Additives Ltd., UK) is a synthetic clay with chemical formula Na₀.7[(Si₈Mg₅.5Li₀.3)O₂₀(OH)₄]₀.7 [16]. Its specific surface area, determined by nitrogen adsorption measurements, is 370 m²/g and its density is ≈2.53 g/cm³. Laponite is composed of charged disk-like sheets with thickness ≈1 nm and average diameter ≈ 25–30 nm. 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 [17]. The negative surface charge of laponite RD, defined as its cation exchange capacity (CEC), was equal to 0.75 meq/g.

For visual characterization of CNTs and CNT+laponite hybrid particles, their transmission electron microscopic (TEM) images were recorded using FEI Technai G2 (200 kV and LaB₆ as a cathode) instrument. Aqueous suspensions of nanoparticles were sonicated during 2 min in Elmasonic S10 H (Elma, Hans Schmidbauer GmbH & Co. KG) device. One drop of suspension was put on Lacey carbon and was dried in open air.

The electrokinetic potential, ζ, was determined using ZetaSizer NS (Malvern, UK) device. Determination of the electrophoretic mobility is based on the Doppler-effect. The program used in this instrument converts the electrophoretic mobility of particles into electrokinetic potential using the classical Smoluchowsky formula. This procedure is acceptable for our systems with relatively big particles/long threads and thin double layers, i.e. for which the contribution of the electrical double layer polarization to the electrosurface
phenomena can be neglected. The values of $\zeta$ indicated below typically represent an average from three-five individual measurements. Before measurements, the suspensions of CNTs and laponite in distilled water were sonicated during 30 min at 35 kHz in the ultrasonic bath (Tesla, Czech Republic). Then hydrochloric acid or sodium hydroxide was used for adjustment of pH values and KCl, CaCl$_2$ and AlCl$_3$ were used as electrolytes.

The preliminary investigations showed the presence of some changes in $\zeta$-potential after preparation of suspensions. However, these dependencies got stabilized after 60 min, the constant values of $\zeta$-potential were acquired, and all presented data correspond to the time $t = 60$ min.

Each experiment was performed, at least, three times in order to determine the mean values and the mean square errors.

2. Experimental Results and Discussion

Figure 1 shows example of high resolution TEM image of a typical CNT (Figure 1a) and CNT+laponite hybrid particles (Figure 1b). It can be seen that the inner and outer diameters of the presented CNT were $\approx 5$ nm and $\approx 10$ nm, respectively and the number of walls was 7 (Figure 1a). In hybrid CNT+laponite systems the laponite platelets are localized on the surface of individual CNTs (Figure 1b).

Preliminary experiments showed that at $X \geq 0.5$ hybrid suspensions were stable against sedimentation. In further electrokinetic experiments the stable hybrid suspensions with optimal ratio of the components, $X = 1$, were used.

Figure 2 shows the pH dependencies of the electrokinetic potential, $\zeta$, of CNTs, laponite platelets and CNT+laponite hybrid nanoparticles in distilled water. All nanoparticles under study were charged negatively in the whole interval of pH values ($\text{pH} = 2$–12). The step-like run of $\zeta$-potential of CNTs versus pH was observed: there was a steep increase of $\zeta$-potential at pH below 4 and above 8, and the $\zeta$-potential was nearly constant ($\zeta \approx -30$ mV) in the interval of pH 4–8. Such behaviour may reflect the changes in the surface charge density and indicate the presence of carbonyl functional groups and phenolic hydroxyls with pK$\approx 2$–3 and 10, respectively, which is in full correspondence with the data of IR spectroscopy [15].
Figure 1. High resolution TEM image of CNT (a) and CNT+laponite hybrid nanoparticles at mass ratio $X = m_L/m_{CNT} = 0.5$ (b). Arrows shows the localization of laponite platelets on the surface of CNTs.
The ζ-potential of laponite platelets at pH > 8 reached constant value. The observed changes may be explained by the impact of pH on the positive surface charge at the edges of laponite. These charges are generally screened by the diffuse part of the electric double layer (EDL) of laponite faces and decrease with pH increase and get neutralized at pH > 11 [17].

The behaviour of ζ-potential of CNT+laponite hybrid nanoparticles (X = 1, C_{CNT} = 0.01 wt %) at different pH value looks like that of CNTs suspension, but it has more negative value at pH > 4, and ζ-potential have constant value at the pH interval 5–10 (ζ ≈ -42 mV). At pH > 10 the ζ-potential value of CNTs and CNT+laponite hybrid particles are the same. The observed behaviour of the ζ-potential can reflect immobilization of laponite platelets on the surface of CNTs.

The observed hetero-coagulation and formation of CNT+laponite hybrid particles evidently reflect the presence of attractive interactions between similarly charged species. Many theoretical and experimental works have reported that unusual attractive interactions can exist for similarly and highly charged colloidal particles (see, [18] for a review). The hetero-coagulation between similarly charged CNTs and laponite platelets can be related to highly heterogeneous distribution of the negatively charged functional groups on the surface of CNTs. The laponite platelets can be effectively immobilized on the neutral portion of CNT surface due to strong attractive electrostatic image forces between the charged particles and neutral graphite-like surface. From the other side, such hetero-coagulation can be also resulted from difference in ζ-potential value of laponite and CNT particles [19]. It should be noted that attractive interaction between negatively charged functional groups of CNT and positively charged edges of laponite are also presented.

Addition of KCl to the CNT suspension gives an initial increase (up to 6.6·10^{-3} mol/dm³ KCl concentration) and then a decrease of the ζ-potential value (Figure 3a). The
presence of maximum at low ionic strengths of solution has been observed previously in different systems and it may be attributed to the influence of surface conductivity (i.e. the EDL polarization) on electrophoresis (see [20] for details).

Addition of a small amount of KCl (< 5 · 10^{-4} mol/dm^3) to laponite suspension results in insignificant decrease of the \( \zeta \)-potential value, whereas increasing concentration of KCl (up to 5 · 10^{-2} mol/dm^3) does not change substantially the \( \zeta \)-potential value of laponite platelets and at high KCl concentrations it turned to be equal to the \( \zeta \)-potential value of laponite particles in pure laponite suspension (\( \approx -45 \) mV). The laponite clay platelets bear considerable negative surface charge (CEC \( \approx 0.75 \) meq/g, \( \zeta \approx -45 \) mV), and their surface is strongly hydrated due to formation of H-bonds by water molecules with functional groups and hydrated Na\(^+\)-ions on the surface. So, discussing the influence of electrolytes on the \( \zeta \)-potential of laponite particles several effects should be taken into consideration.

Addition of KCl to laponite suspension results in an ion exchange in the EDL, i.e. substitution of the surface Na\(^+\)-ions by less hydrated, with higher adsorption affinity K\(^+\)-ions. It is accompanied by a decrease in hydration of the surface and shift of the shear plane toward the surface, i.e. by an increase of the \( \zeta \)-potential value. With rising the KCl concentration the compression of the double layer increases, which gives a decrease of the electrokinetic potential. At the same time, an increase in the ionic strength at high electrolyte concentrations leads to destruction, thinning of the hydrate layers; dehydration of the surface results in an increase of the electrophoretic mobility. Such combination of these effects leads to non-conventional shape of the \( \zeta(C) \) curve for KCl shown in Figure 3a.

The run of the \( \zeta \)-potential of CNT+laponite hybrid nanoparticles at addition of KCl electrolyte (Figure 3a) is complex. An increase of KCl concentration up to \( C_{KCl} < 5 \cdot 10^{-4} \) M gives a decrease in the \( \zeta \)-potential value, and at \( C_{KCl} > 1.7 \cdot 10^{-2} \) M increasing \( \zeta \)-potential values were observed; similar behaviour of \( \zeta \)-potential was observed for CNTs-containing suspension. At concentration of KCl \( C_{KCl} = 5 \cdot 10^{-2} \) M the \( \zeta \)-potential increased and stabilized at \( \approx -35 \) mV up to \( C_{KCl} = 1.7 \cdot 10^{-2} \) M.
Addition of bivalent counter-ions results in considerable decrease of the \( \zeta \)-potential values (Figure 3b) and trivalent counter-ions cause charge reversal of the carbon nanotubes (Figure 3c). Such dependencies were obtained for a large number of different disperse systems [20]. Thus, we can state that carbon nanotubes behave in external electric field like typical hydrophobic colloidal systems.

Similarly, there are no substantial changes in the \( \zeta \)-potential of laponite particles at low (< 5 \( \times \) 10^{-3} mol/dm^3) CaCl\(_2\) (Figure 3b) or AlCl\(_3\) (Figure 3c) concentrations in suspension. It can be explained by existence of thick, protective hydrate layers on the surface of particles; a marked effect of adsorption of counterions on the EDL structure, i.e.\( \zeta \)-potential value, is observed at relatively high concentrations of electrolyte, at which surface hydrate layers are partially destroyed and much thinner. Sharp decrease of the \( \zeta \)-potential value of laponite particles takes place at much higher levels of bivalent, and trivalent ions than that typically observed for hydrophobic particles. The rise in concentration of trivalent Al\(^{3+}\)-ions results

---

**Figure 3.** Electrokinetic potential, \( \zeta \), of CNTs (\( C_{\text{CNT}} = 0.01\% \) wt), laponite platelets (2.0% wt) and CNT\_laponite hybrid nanoparticles (\( C_{\text{CNT}} = 0.01\% \) wt, \( X = 1 \)) versus concentration of electrolyte, \( C \), of KCl (a), CaCl\(_2\) (b) and AlCl\(_3\) (c)
in substantial decrease of the electrokinetic potential, and then an inversion of its sign, as it is typical for hydrophobic colloids and CNTs themselves.

It is interesting to note that the behaviour of CNT-laponite hybrid nanoparticles while adding electrolytes with bivalent (Figure 3b) and trivalent (Figure 3c) cations is the same as for the CNTs suspension. This testifies that the effect of adsorbed/adagulated laponite particles on the EDL parameters of CNT-laponite hybrid particles is relatively weak. At the same time the CNTs+laponite suspensions at optimal ratio of the components, \( X = 1 \), were stable against sedimentation. This evidenced that stabilization of CNTs suspension by laponite nanoparticles is caused mainly by non-electrostatic effects, e.g., steric stabilization, hydrophilization of the surface etc.

Thus, there is a marked distinction between the effects of laponite on CNTs in electrolyte solutions in comparison to hydrophobic particles, i.e., no effect on the electrokinetic potential at low concentrations and a steep decrease in the \( \zeta \) value or its inversion at relatively high (higher than that in hydrophobic colloid [21]) content of the electrolyte. This can be explained by strong hydration of the surface of particles: substantial changes in the electrokinetic potential may take place in the case of partial destruction of the stabilizing hydrate layers.

**Conclusions**

The electrokinetic potential of carbon nanotubes and laponite as well as carbon nanotubes+laponite hybrid particles was measured as a function of pH and electrolytes concentration. It has been shown that the electrokinetic behaviour of carbon nanotubes resembles that of the lyophobic colloids. An increase in pH from 2 to 12 resulted in substantial increase of the absolute (negative) values of the zeta potential of carbon nanotubes due to dissociation of surface hydroxyl and carbonyl groups, which was identified by infra-red (IR) spectroscopy. The observed attraction between similarly charged colloidal particles of carbon nanotubes and laponite can be explained by the highly heterogeneous distribution of negatively charged functional groups on the surface of carbon nanotubes and difference in zeta potential of nanotubes and laponite particles.

**Acknowledgement**

*This research was (partially) carried out in the framework of the cooperation agreement between the Hungarian Academy of Sciences and National Academy of Sciences of Ukraine. Authors thank Peter Pekker for help with HRTEM images.*

**References**


