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Zeta Potential of Modified Multi-walled Carbon Nanotubes in Presence of poly (vinyl alcohol) Hydrogel

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The main objective of this study is investigate the behavior of the Zeta Potential of the MWCNT modified with SDS(Sodium Dodecyl Sulfate) and CTAB(Cetyl Tetraethyl Ammonium Bromide) in presence of PVA. Full hydrolyzed PVA was used. As a result, adding PVA in the CNT solution led to decrease the Zeta Potential. The Zeta Potential of suspended colloid varied from 42.00mV to 6.48mV and -45.00mV to -6.4mV at 1.5% concentration of PVA; according with the changing pH, the Zeta Potential dropped to near zero at pH 3 and 11. The pH and PVA has strong influence in the reduction of ZP of MWCNT solution. MWCNT-PVA solution with 33.30mV, -35.69mV at 0.01% of PVA was exposed under AC field; a uniform coat was obtained, with the SDS-MWCNT-PVA solution.

Keywords: PVA, MWCNT, CTAB, SDS, Zeta potential

1. INTRODUCTION

Since the Nanotubes were discovered, have been widely used because their atomic structure, good mechanical, thermal and electrical properties. Moreover, Nanotubes are gaining special interest in Biomedical, Aerospace, Electronics and Biosensor applications [1, 2]. CNT have been embedded into polymer matrix as conductive filler; however the first challenge in the process of producing this composite is obtain a good dispersion of the filler within the polymer matrix.

Mechanical (sonication) and chemical methods have been study to disperse CNT. The dispersibility of the CNTs was study by analysis of the zeta potential [3].

Surface modification of materials started in early 1990's with Badley, who modified the surface of a colloidal material. Since then, modified silica nanoparticles, surface modification have been widely used in real applications. The importance of the Zeta Potential is an essential part of different applications as Electroosmosis, flocculation and stability of CNT. The advance in the study of solid-liquid interface electrical properties has led to the development of new techniques. The electrophoresis, electro-osmosis and streaming are the three electrokinetic effects using for development the zeta potential [4].

When fluid flows across a solid surface, the surface of the solid may become charged. Ions of opposite charge in the liquid medium, are attracted to the surface in order to neutralize the surface charge creating what is commonly referred to as an electric double layer (EDL). The strength and polarity of the EDL is represented by the parameter known as the Zeta potential. The value of Zeta Potential changes according to the pH or electrolyte concentration, beside the kind of polymer [5–7].

For its good biodegradability, incompatible, chemical and oil resistance, non-toxic, non-carcinogenic, water soluble, non-expensive and excellent mechanical properties (high flexibility and tensile strength), excellent emulsifying, film forming and adhesive properties as well as oxygen and aroma barrier properties PVA has importance in applications fields like biomedical materials, biosensor, electrochemical sensors, membranes with selective permittivity, viscous medium for controlling the crystallization process of salts, controlled drug delivery or catalytic systems [8–11]. The characterization of zeta potential has been studied in relation between of EDL in the mix of PVA with kaolinite, peat, chitosan and lipid nanoparticles [12–14].

The main objective of this study is investigate the behavior of the Zeta Potential of the MWCNT modified with anionic and cationic surfactants in presence of PVA (different concentration of PVA was tested), also to produce an homogeneous film of PVA-CNT applying AC field.

2. MATERIALS AND METHODS

MWCNT (60-100nm) were purchased from Shenzhen Nanotech Port Co. Ltd. The surfactant investigated were CTAB (Cetyl Trimethyl ammonium Bromide) (Xilong Chemical, Guangdong, China) and SDS (Sodium Dodecyl Sulfate) (Beijing Hong Xing Chemical), Polyvinyl Alcohol-PVA (Full hydrolyzed) as a polymer matrix was received from Beijing Xisi Chemicals Co. Ltd and Distilled water was used as a solvent.

2.1 MWCNT Dispersion

The dispersibility of CNT was measured in different surfactant solutions (Cationic surfactant-CTAB and anionic surfactant-SDS). 35mg of MWCNT were mixed in 20ml of CTAB and SDS

solution, the surfactant concentration varied from 5mg to 35mg. The CNT surfactant dispersion was sonicated at 90Hz for 15 min using a JY92-II ultrasonic Cell Pulverized. Then the solution was settled at room temperature for 24 hours to get natural sedimentation.

2.2. Multiwall carbon nanotubes-PVA preparation

PVA solution was prepared at 5% using a YX-280 pressure steam sterilizer, heated up to 120° C for 2 hours. The stable solution of SDS-MWCNT (1:1) and CTAB-MWCNT (1:1) was mixed with PVA solution, therefore the final solution of CNT-Surfactant had 0.01%, 1% and 1.5% of PVA, and this solution was mixed through sonication at 90Hz for 30 minutes in a JY92-II ultrasonic Cell Pulverized.

2.3. Zeta Potential Measurement and Electrophoretic Deposition

To Determine the Zeta Potential and mobility measurements of MWCNT modified with CTAB and SDS as well as MWCNT-PVA solution were using a Delsa Nano-Particle Analyzer model A54412AA. The instrument employs Smoluchowski's Equation 1 to determine the electrophoretic mobility of the particle and subsequently convert it in the Zeta Potential [15, 16].

$$\zeta = \frac{\mu\sigma}{\epsilon\epsilon_0} \frac{\Delta V}{\Delta P} \quad (1)$$

The Smoluchowski's Equation employs four known parameters: viscosity (μ), conductivity (σ), permittivity ($\epsilon\epsilon_0$), and linear fits to the pressure-voltage curve.

The Zeta Potential of the MWCNT, was measured as function of the concentration of the surfactant and PVA concentration. In order to analyzed the behavior of the MWCNT-PVA solution in relation of the pH changing, solution of HCl (0.5%) and NaOH (0.5%) was used for adjusting the value pH in the range of 3-11. The solution of CNT-PVA with the highest zeta potential is used for EPD.

EPD was carried out under room temperature and certain parameter conditions (ZP, MWCNT concentration, field strength, time deposition and distance between the substrate electrode), in order to establish the optimal conditions. The Electrodes in EPD were made of 304 Stainless Steel (10mm • 20mm • 1mm). The electrodes were sonicated 15 minutes with ethanol and distilled water to clean them. The two electrodes were fixed parallel at 1cm distance in the suspension. The signal used were rectangular pulses with 70% duty cycle, the frequency value was: 1Hz and the instrument used was a Function Generator model GFG-8016D. The time of exposure was 3, 5, 10 and 15 minutes. The samples were exposed at cross-linking by thawing-freezing method, 3 cycles were used, each cycle consist in 8-hours freezing and 8-hours thawing, then the samples were kept in ambient conditions until the analysis test was made.

3. RESULTS AND DISCUSSION

3.1 Multiwall Carbon Nanotubes Dispersion

The structure of surfactants is very diverse and their nature defines the efficiency of the dispersion of CNT in solution. Surfactant molecules containing aromatic groups are capable of forming more specific and more directional ($\pi-\pi$) stacking interactions with the graphitic surface of nanotubes [7, 11].

When the surfactants are dissolved in water, cation and anion are forming according with the nature surfactant, then they are absorbed in the CNT surface, where the negative and positive change lead to electrostatic repulsion between the molecules, and stabilize the nanotubes colloids.

The surface of the CNT was modified using different concentration of CTAB and SDS as cationic and anionic surfactant, in presence of sonication. Low concentration of surfactant showed poor CNT dispersibility, revealing agglomerations of MWCNT bundles. While a high concentration surfactant, gives high encapsulation on MWCNT surface and provides good dispersion as well as low sedimentation.

The Figure 1 shows the behavior of dispersion of the CNT in presence of different SDS and CTAB concentrations. The dispersion of the MWCNT, increase gradually with the concentration of surfactant. A stable solution of CNT is obtained when the relation CNT to surfactant is 1:1 (Figure 1-a, and Figure 1-e).

In the Figure 1-b, Figure 1-d, agglomeration of CNT can be observed, due to small concentration of the surfactant, this behavior can be attributed to the low absorption of the surfactant molecules on CNT surface.

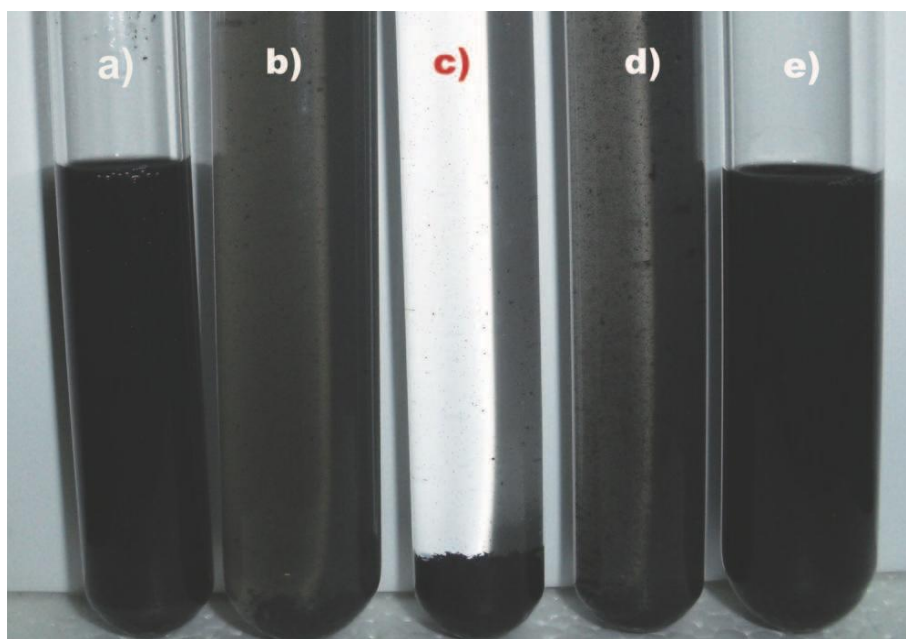


Figure 1. Dispersion of MWCNT (35mg/20ml) in different concentrations of CTAB and SDS: a) 35mg-CTAB, b) 5mg-CTAB, c) without surfactant, d) 5mg- SDS, e) 35mg-SDS

In order to develop a stable solution of CNT, is necessary to control the concentration or the surfactant, quantity of CNT, temperature, pH as well the dispersion method(sonication). The last parameter involves complex physicochemical interactions that can result in either cluster breakdown or further agglomeration. When the suspension is subject to the ultrasonic treatment, certain energy is delivered in the suspension, this energy depends of the applied power and the total exposure time under sonication treatment.

If CNT suspension is exposed under sonication considering the same power, same quantity of surfactant and MWCNT, but at different dispersion time, the CNT solution going to presents different dispersion state.

3.2 Zeta Potential of MWCNT-Surfactants

According to the DLVO (Derjaguin-Landau-Verwey-Overbeek) Theory, a potential barrier between surface-charged particles in suspension may result in colloidal meta-stability. The van der waals forces, as well as repulsion caused by the overlap of the electric double layer (EDL) around each particle. The double layer is formed in response to active surface group dissociation, of charged species on the surface [19].

The Figure 2 and Figure 3 show the ZP of MWCNT as a function of the CTAB and SDS quantity. The Zeta Potential increase gradually, with the surfactant concentration. The SDS-MWCNT has -42.65mV and CTAB-MWCNT 49.51mV respectively. This is attributed to the absorption of cationic and anionic charge on the carbon nanotubes surface.

After using 5mg SDS/CTAB the Zeta Potential become more negative/positive and presented an increase in magnitude of -27.230mV to -42.65mV for SDS and -19.380mV to 49.51mV for CTAB.

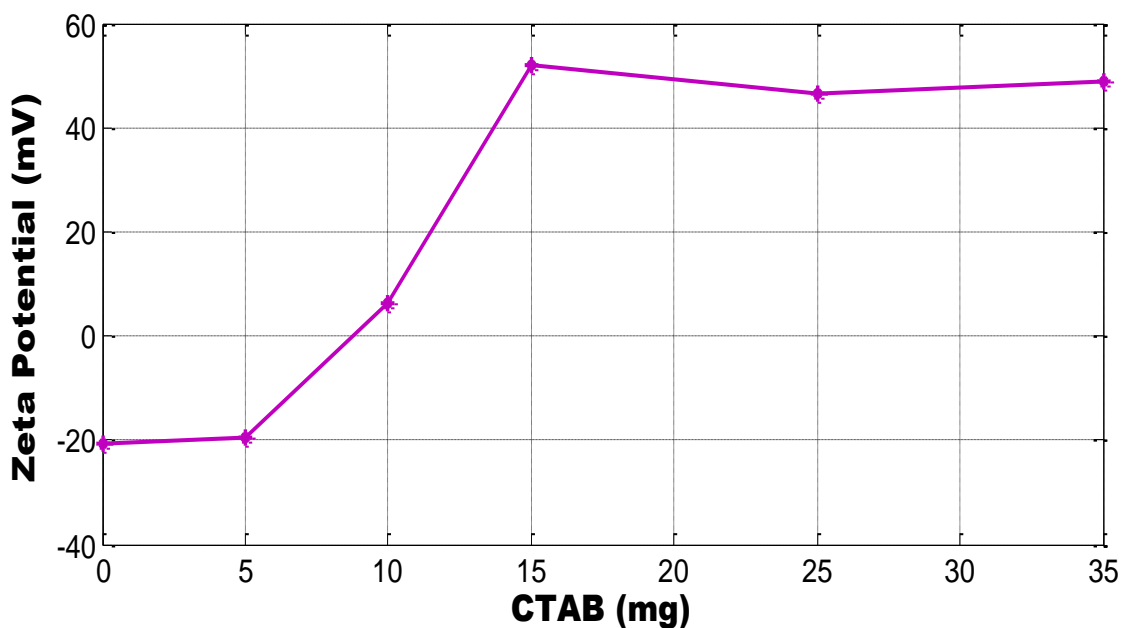


Figure 2. Zeta Potential of MWCNT modified with CTAB

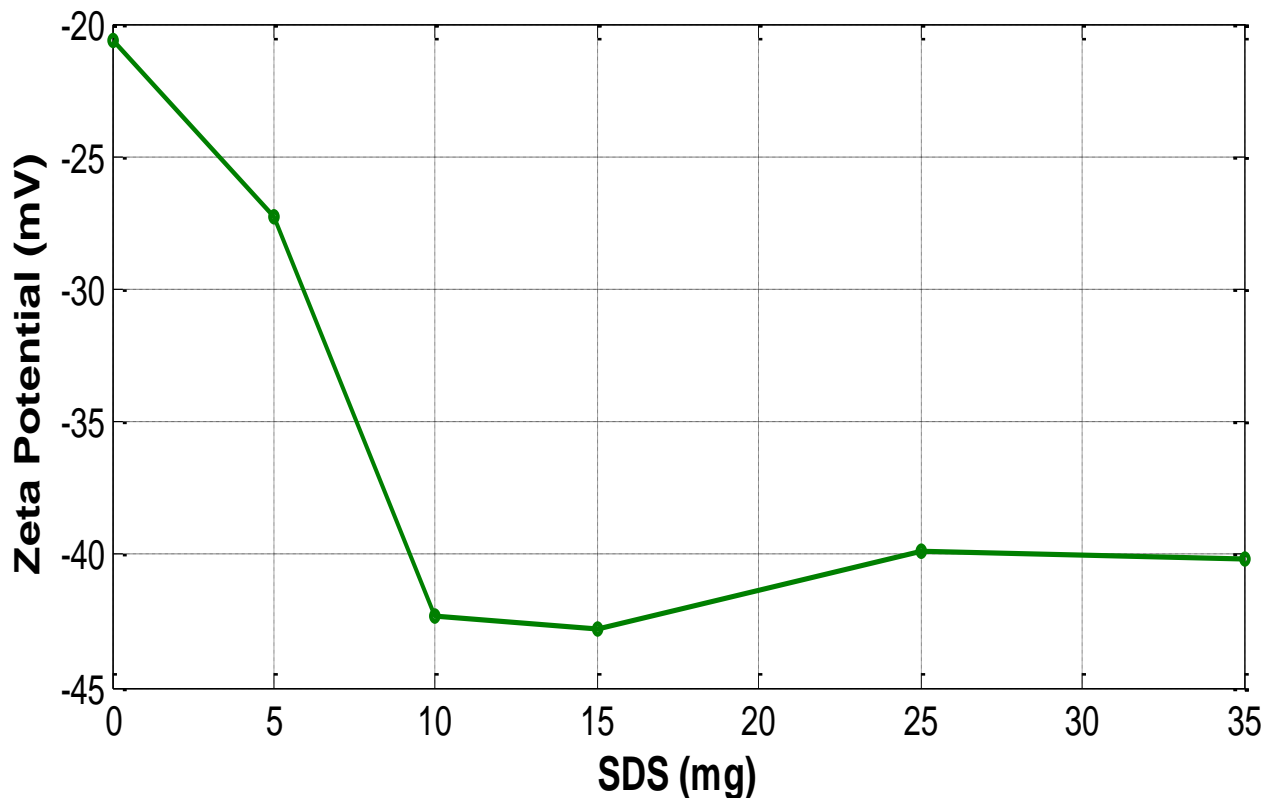


Figure 3. Zeta Potential of MWCNT modified with SDS

The experiments indicate that the MWCNT have a preference to bind with CTAB rather than SDS; because even using the same concentration and the same level of dispersion, the solution CNT-CTAB presents higher ZP and is more stable. The measurement of the ZP was carried out at pH 6.3 and 6.2 for SDS and CTAB respectively. Any change in the solution pH, affects the ZP value.

3.3 Zeta Potential of MWCNT-Surfactant without PVA

The behavior of the Zeta Potential of MWCNT in presence of basic and acid medium is shown in the Figure 4 and Figure 5. It shows that the ZP of MWCNT is affected by the addition of acid or basic solutions. The ZP of the SDS-MWCNT varied from -42.65mV to -19.92mV with pH 6.2 and 3, when an acid solution is added. The ZP values changes from -42.65mV to -35.95mV in presence of basic medium.

While CTAB-MWCNT moved on 49.51mV to 6.39mV with pH 6.3 and 3 and 49.51mV to 2.23mV with pH 6.3 and 11 respectively. Is clear that the CTAB-CNT solution is more sensitive to change in medium basic/acid, respect to SDS-CNT solution.

This variation in the zeta potential can be attributing to the energy electrical field in the MWCNT surface surrounded by the surfactant.

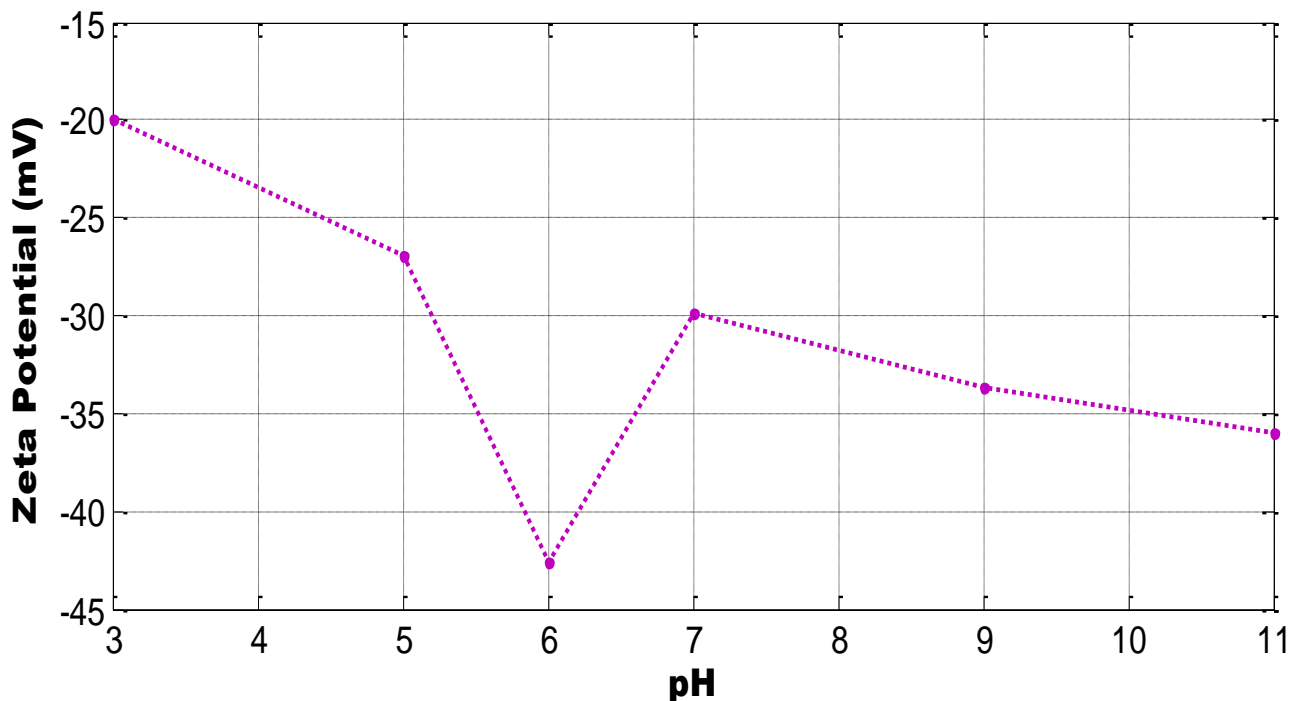


Figure 4. Behavior of Zeta Potential of MWCNT-SDS at different ph

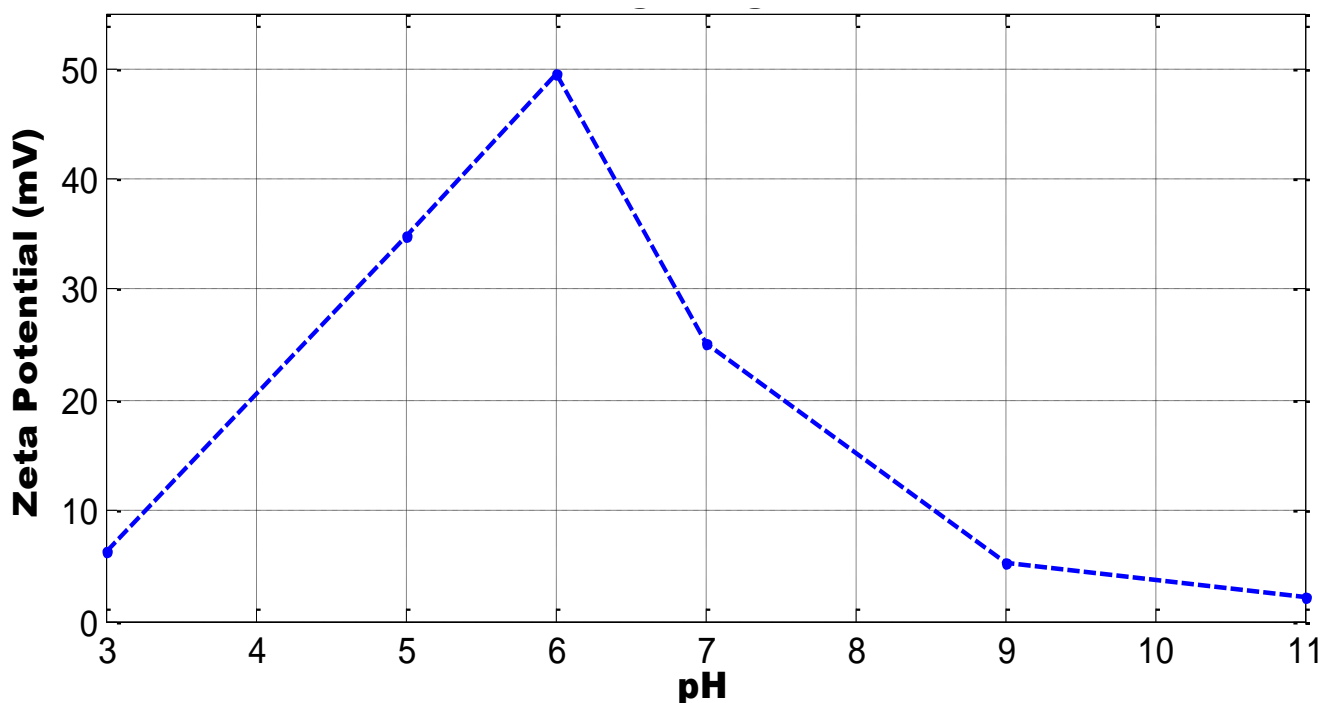


Figure 5. Behavior of Zeta Potential of MWCNT-CTAB at different ph

The CNT solutions present change in the negative ZP and positive ZP when acid o basic solution is added. The positive and negative charge on the CNT surface is constant at any pH value. The initial pH of the MWCNT-SDS and MWCNT-CTAB was 6.3 and 6.2.

3.4 Behavior of MWCNT-Surfactant in presence of PVA

The Zeta Potential of the CNT solution, also can be affected by the PVA concentration as is shown in the Figure 6 and Figure 7.

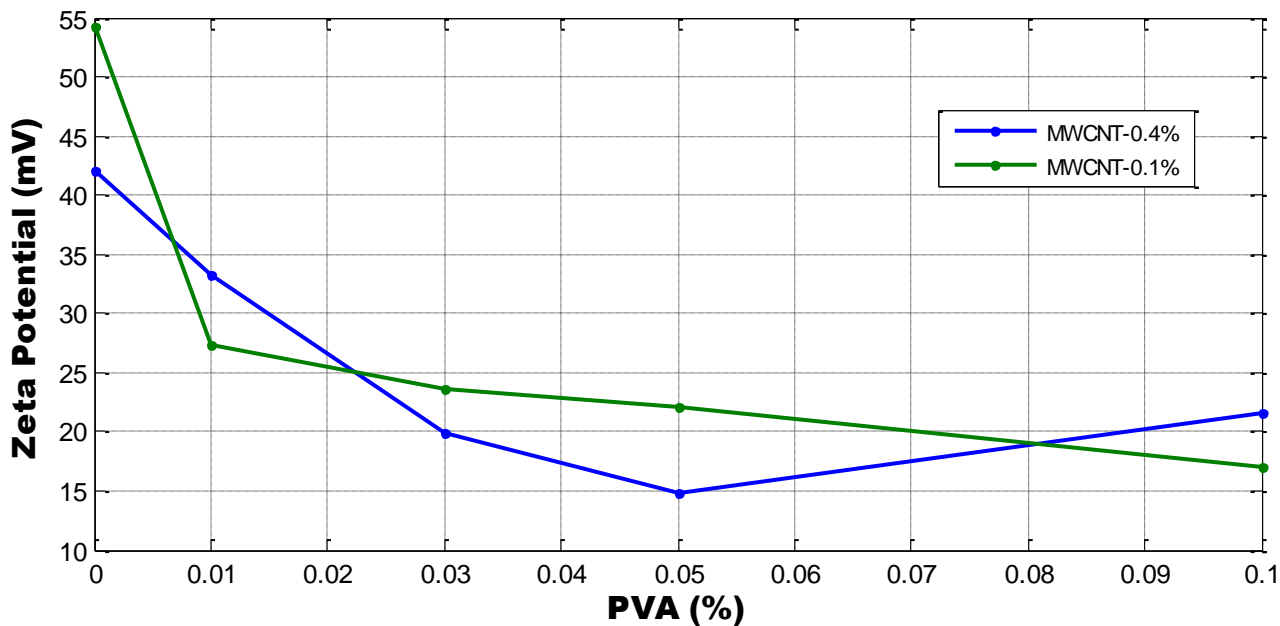


Figure 6. Effect of PVA on Zeta Potential of MWCNT-CTAB at different % of MWCNT

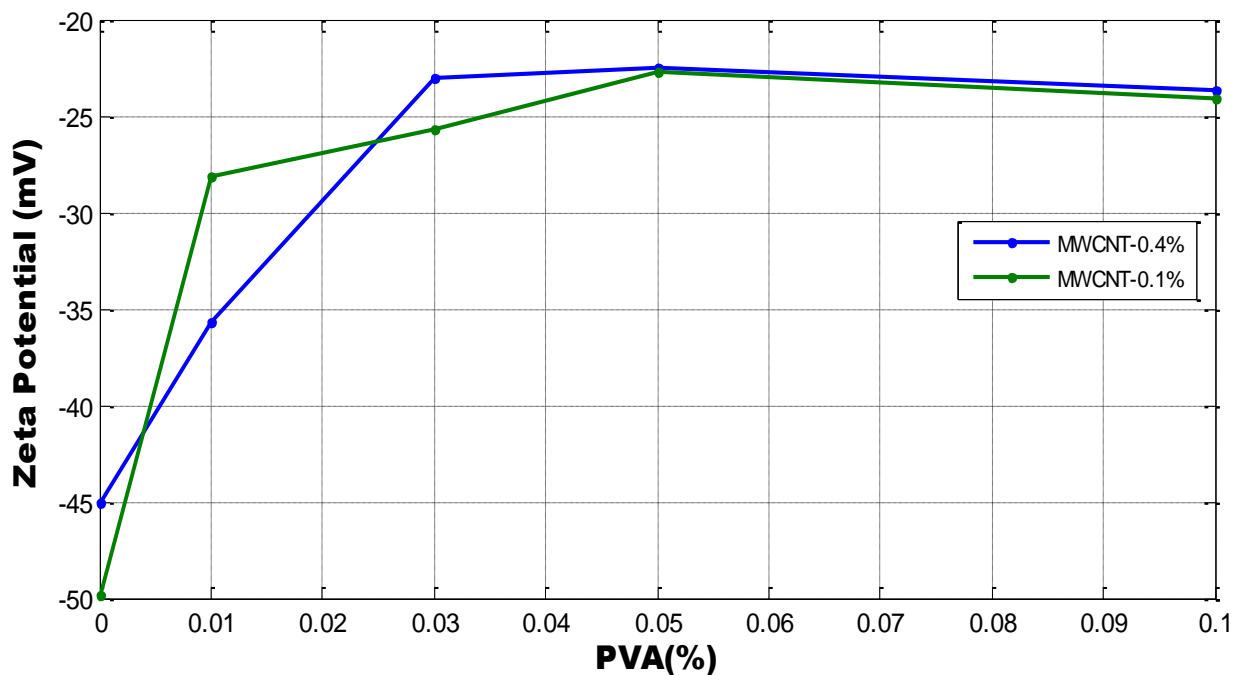


Figure 7. Effect of PVA on Zeta Potential of MWCNT-SDS at different % of MWCNT

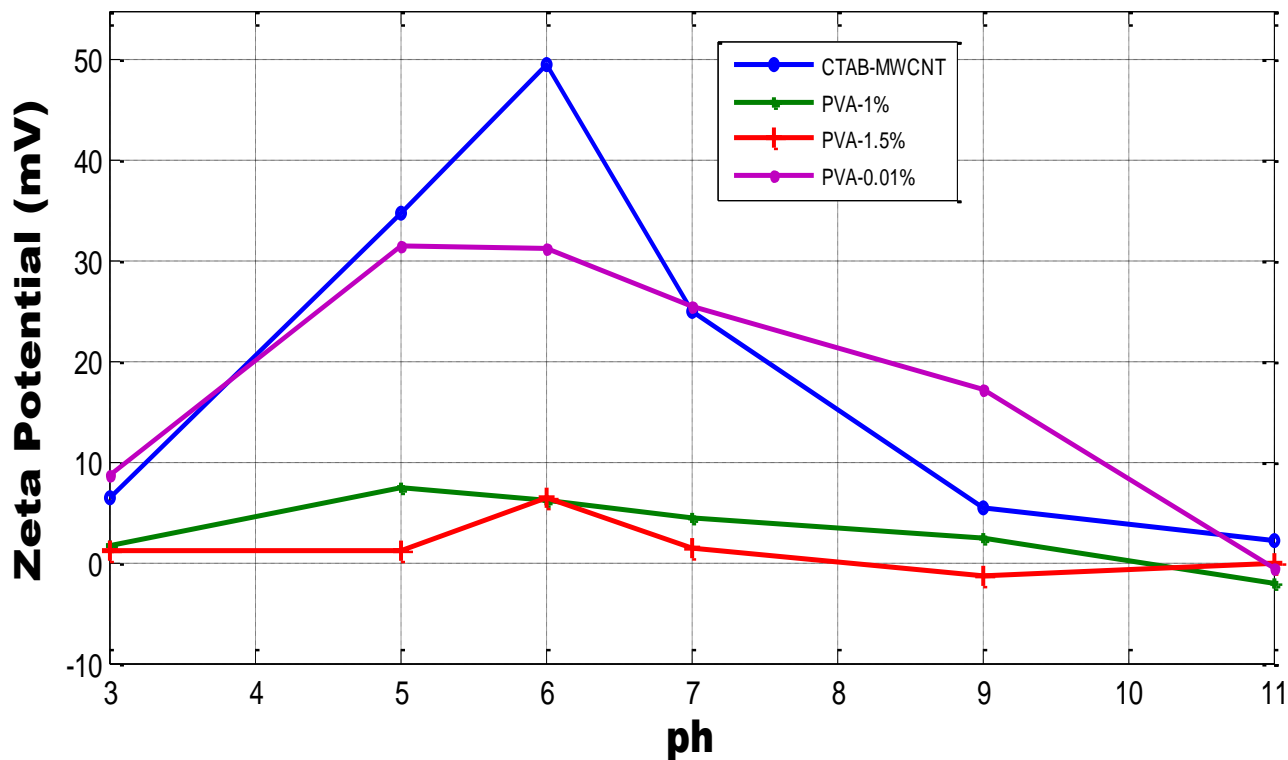


Figure 8. Effect of PVA on Zeta Potential of MWCNT-CTAB

The CNT solution was prepared at 0.4% and 0.1% of CNT, reduction in the ZP value is observed when PVA solution is added into the CNT solution. The initial ZP was 42.00mV, 54.29mV, -45.00mV and -49.88mV respectively.

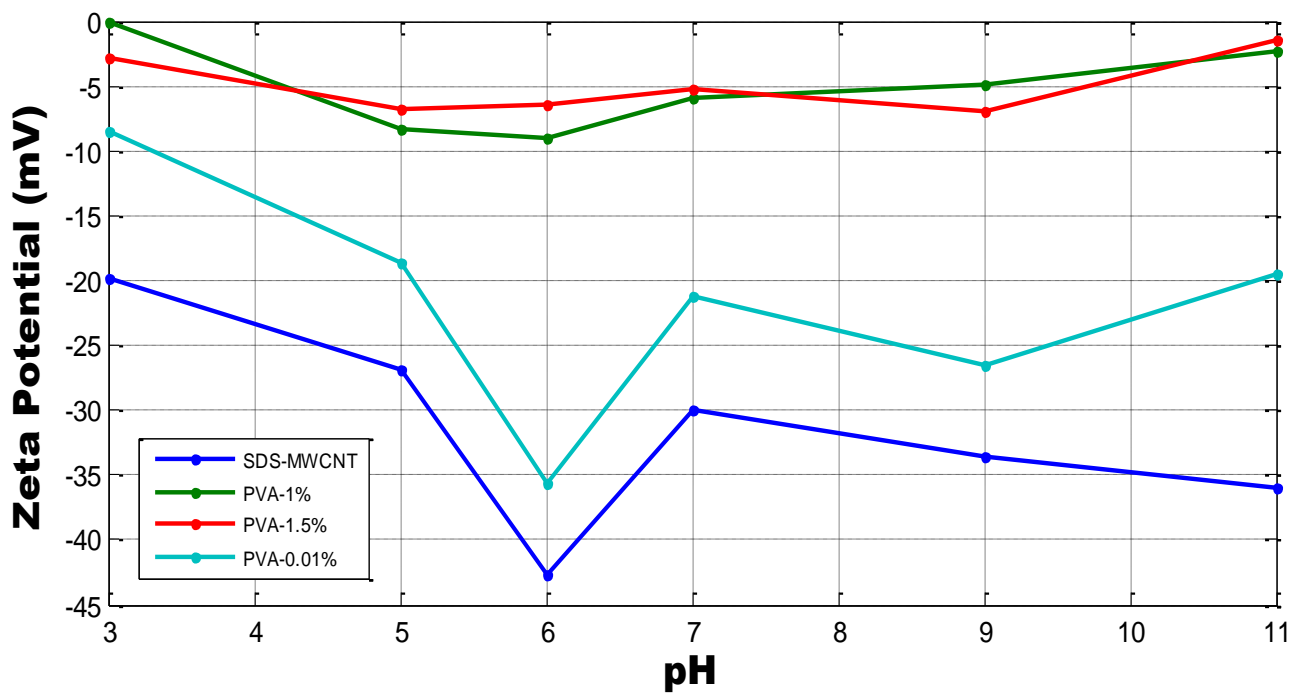


Figure 9. Effect of PVA on Zeta Potential of MWCNT-SDS

The ZP for MWCNT-CTAB varied from 42.00mV to 21.60mV and 54.29mV to 16.99mV, when the PVA concentration is 0.1%. SDS-MWCNT solution presented similar behavior, the ZP varied from -45.00mV to -23.67mV and -49.88mV to -24.07mV at 0.1% of PVA. While at 0.01% of PVA, the ZP shift at 33.30mV, 27.37mV, -35.69mV and -28.1mV. It is clear that PVA concentration has strong influence in the ZP reduction, when it is absorb on the MWCNT surface.

The Figure 8 and Figure 9 show the behavior of the ZP of MWCNT-PVA at different pH, 0.01%, 1% and 1.5% of PVA are considered, also a CNT solution at 0.4%.

The solution of MWCNT-SDS and MWCNT-CTAB has a natural pH of 6.2 and 6.3 respectively. The ph of the CNT solution doesn't present change, in addition of PVA. At this pH, the ZP of the MWCNT-PVA is 33.30mV, 6.15mV and 6.48mV and -35.69mV, -8.99mV and -6.4mV at 0.01%, 1% and 1.5% of PVA.

The ZP of MWCNT-SDS-PVA, decrease to -8.48mV, 0.16mV and -2.91mV in medium acid, in addition of basic solution the ZP values are -19.43mV, -2.38mV, -1.46mV. While the ZP of MWCNT-CTAB-PVA in acid and basic medium decreased to 8.67mv, 1.67mv, 1.14mV and -0.69mV, -2.13mV,-0.19mV.

The concentration of the PVA and pH, has strong influence in the reduction of the Zeta Potential of MWCNT-PVA solution, this behavior could be attributed probably to the nature medium. The CNT-PVA solution presents negative and positive charge. The pH reduces the electrostatic repulsion between the positive/negative charged surfaces and dissociated in PVA macromolecules. The PVA take place on the CNT surface it which could be responsible of the reduction of the zeta potential [20].

3.5. Isoelectric Point of MWCNT-Surfactant in presence of PVA

The Isoelectric Point (IEP) is defined as the pH value at which the electrokinetic potential equals to zero; the points of zero charge (PZCs) are defined as the pH values, at which one of the categories of surface charge equals to zero [21]. The behavior of the IEP on PVA solution in different solid particles has been studied [20, 22].

The PVA has different adsorption mechanisms depending of the type of particle, medium and the degree of the hydrolysis of PVA.

The IEP of CNT solution is shifted when the PVA is absorbed on the surface, also changes with the pH value. 1.5% of PVA in CNT solution have a ZP value (6.48mV and -6.4mV) near to zero. Similar behavior is observed at pH 3 and 11, the ZP is -2.91mV, -1.46mV for MWCNT-SDS-PVA and 1.14mV, -0.19mV for MWCNT-CTAB-PVA.

3.6. Effect of the Polyvinyl Alcohol on the mobility particles

The Figure 10 and Figure 11 show the mobility behavior of CNT solution with different percentages of PVA. The CTAB-MWCNT has an specific mobility of $2.44\text{E-}04\text{cm}^2/\text{Vs}$, $4.79\text{E-}05\text{cm}^2/\text{Vs}$, $5.06\text{E-}05\text{cm}^2/\text{Vs}$ while the mobility of SDS-CNT is $-1.64\text{E-}04\text{cm}^2/\text{Vs}$, $-7.01\text{E-}05\text{cm}^2/\text{Vs}$.

/Vs, $-4.98E-05\text{cm}^2$ /Vs at 0.01%, 1% and 1.5% of PVA. Is clear the strong influence that the concentration of PVA has in the mobility of CNT particles.

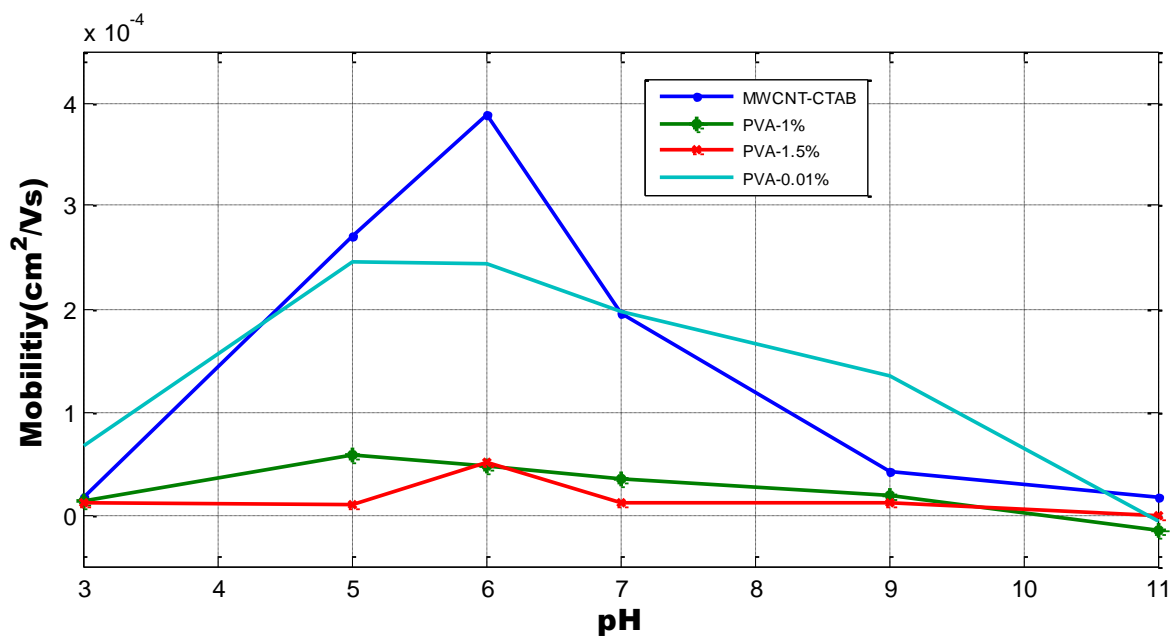


Figure 10. Mobility particle of MWCNT-CTAB in presence of PVA

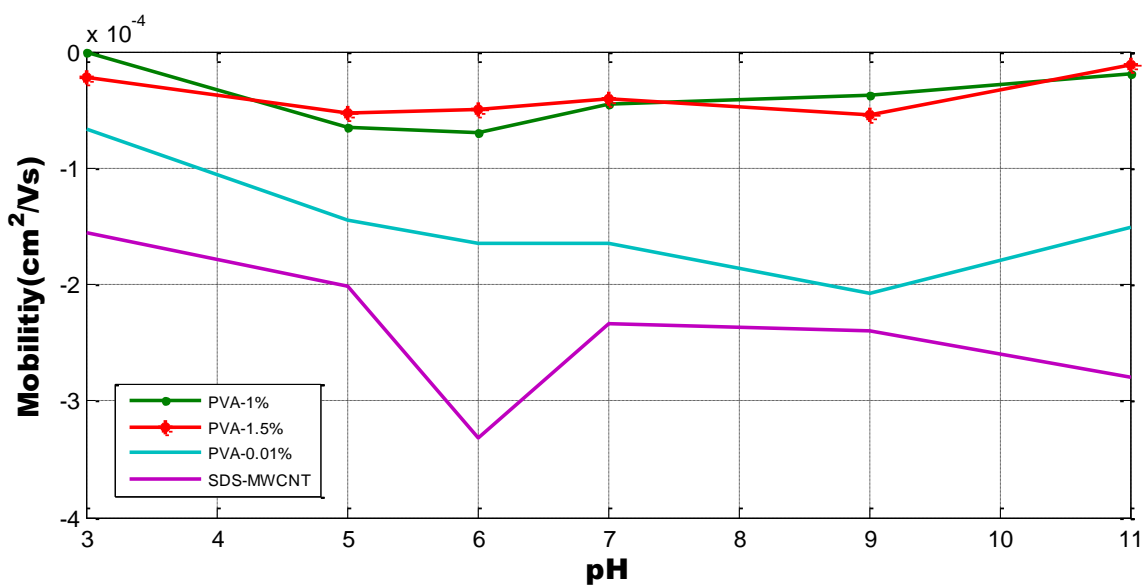


Figure 11. Mobility particle of MWCNT-SDS in presence of PVA

3.7 Electrophoretic Deposition of MWCNT-PVA

The MWCNT-PVA solution with a ZP of 33.30mV, -35.69mV at 0.01% of PVA was exposed under electric field in order to produce a coat homogenous on the electrode surface.

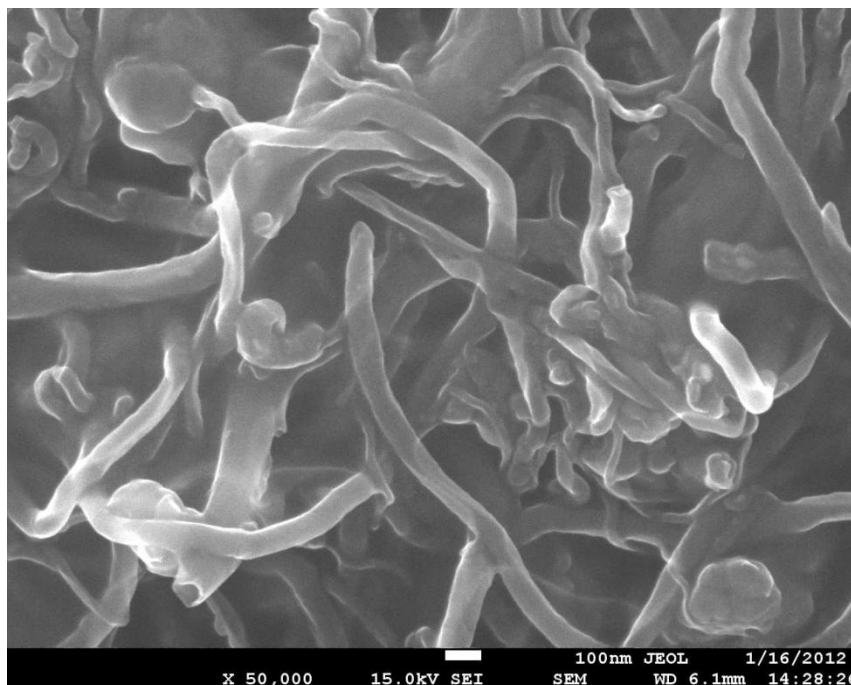


Figure 12. Cross-linking of MWCNT-PVA

When the electric field is applied in the CNT-PVA solution, the MWCNT-SDS-PVA particles moved towards the positive electrode, while the MWCNT-CTAB-PVA particles take place in the negative electrode.

After 10 minutes of exposure to the CNT solution under an electric field, a uniform coat of MWCNT-SDS-PVA is deposited on the electrode surface, while the MWCNT-CTAB-PVA shows difficulty in developing a homogeneous film on the electrode surface. The cross-linking of PVA was made by the Freezing-Thawing method, 3 cycles were used (8-hour freezing followed by 8-hour thawing). Figure 12 shows the cross-linking between the PVA-CNT, horizontal alignment carried out on the film.

Bubbles formation appears during the EPD, this phenomenon is attributed to the hydrolysis of water, which has as a consequence, an inappropriate film deposit. Pulsed DC electric and asymmetric alternating current (AC) electric fields, are receiving special attention [22] in the control of bubbles formation.

Those techniques could be used in future investigations related to CNT-PVA deposition.

4. CONCLUSIONS

This research is focused on the behavior of Zeta Potential of CNT in the presence of SDS/CTAB as well as the change in relation of pH and addition of PVA polymer. The results demonstrate:

- The MWCNT presents negative or positive charge on the surface, depending on the surrounding media used, which is a Cationic (CTAB) or anionic (SDS) surfactant.

- The dispersion of CNT is affected by the quantity surfactant, pH, and temperature and sonication method. Small quantity of surfactant presents a poor dispersion of CNT, while high concentration of surfactant encapsulated of CNT surface given a stable solution, also as consequence a high zeta potential value.

- Is important to keep in mind, without the appropriate sonication is not possible to get the desire CNT dispersion, even if the surfactant concentration is adequate. That means, if CNT suspension is exposing at the same power but with different times of sonication, the CNT going to present different levels dispersion.

- The pH has strong influence in the ZP of MWCNT-Surfactant and MWCNT- PVA. With pH 3 and 11 the solution is near to IEP, for EPD is not convenient to use at MWCNT-PVA with ZP near to the IEP.

- Also the PVA has influence in the reduction of the ZP MWCNT; the IEP of MWCNT is shifted near to zero, when the % of PVA is high in the solution.

- This research showed, if ZP of the PVA-CNT solution is lower than 40mV absolute, is difficult to produce a homogeneous deposit on the substrate.

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