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Colloidal Behaviors of Conducting Polymer/Chitosan Composite Particles

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Abstract

In this study, colloidal behaviours of conducting polymer (CP) and chitosan (CS) multi-functional composite particles were investigated by using electrokinetic measurements. The effects of pH, electrolytes, surfactants and temperature on electrokinetic properties were determined as a function of ζ -potential of the colloidal dispersions. The obtained result showed that the zeta (ζ)-potential of CP increases to the higher positive region due to interaction with polycationic CS. Isoelectric points (IEP) of the CP/CS composite are also shifted to higher pH values. The positive ζ -potential of the composite shifts to more positive regions when the electrolyte valence and cationic surfactant concentration are increased. Also, these ζ -potential value shifts to negative region with the addition of anionic surfactant. Temperature affects the ζ -potential of the CP/CS dispersion. As a conclusion, colloidal behaviours of CP/CS composite particles can be altered by using different charged molecules. Therefore, CP/CS composite particles could be a good adsorbent for separation process.

Keywords: zeta potential, isoelectric point, conducting polymer, chitosan, colloidal particle

1. Introduction

1.1. Electrokinetic properties

Electrokinetic measurements are very useful techniques to present the interactions between dispersed particles in an aqueous dispersion. Electrokinetic properties of materials are also important to prepare sedimentation problems of solved materials. Zeta (ζ)-potential value is a surface charge of colloidal particles in an aqueous solution [1–3] and gives information about

surface groups of colloidal particles and interaction between solid and liquid interfaces. It can be used for determination of some physical properties such as colloidal properties, Particle interactions and synthesis of charged polymeric composites. ζ -Potential cannot be measured directly. It can be determined using electrokinetic techniques, such as streaming current or potential, electric conductivity and electrophoretic mobility [4, 5].

The electrokinetic potential on surface of a solid particle in contact with a polar medium (i.e. H_2O) is controlled by the dissociation of surface groups, the preferential adsorption of cations or anions, the adsorption of polyelectrolytes and surfactants, the isomorphous substitution of cations and anions [6]. Generally, descriptions of the charge distribution at solid/liquid interface assume the presence of an electrical double layer consisting of a fixed (Stern) layer and a diffuse layer [7]. Externally applied electrical force causes a relative movement between these layers (**Figure 1**).

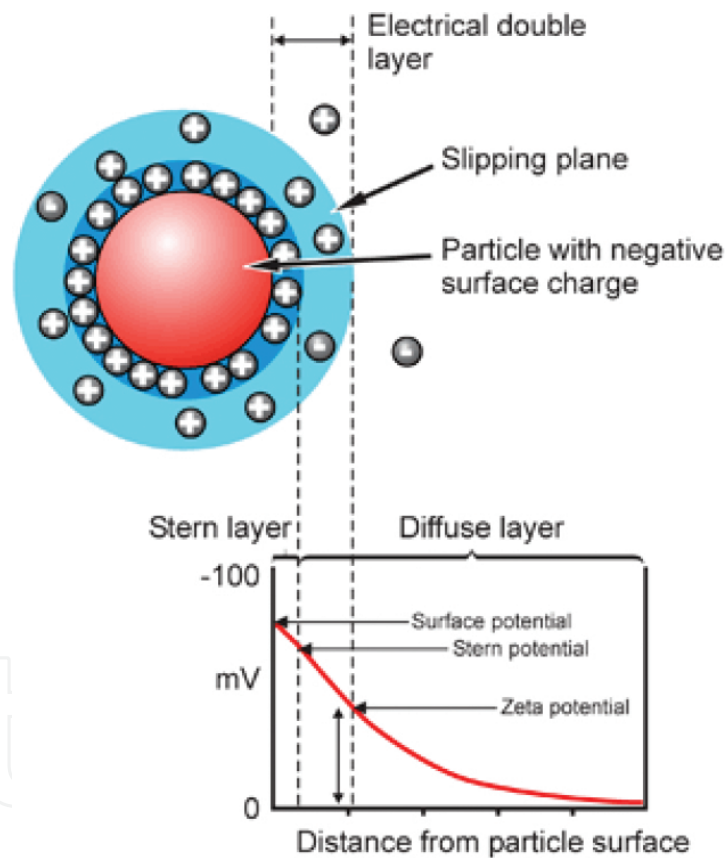


Figure 1. Zeta potential on a charged particle.

The interface between a solid and a solution may be treated as a semi-permeable membrane, which allows only the charged species common to both the solid and the pass through. These species are called potential determining ions and have the ability to affect the sign of the ζ -potential. They are the major ions responsible for establishment of the surface charge of particle. On the other hand, some ions called indifferent ions are adsorbed by electrostatic attraction only thereby affecting the magnitude of ζ -potential and not by the surface potential

[8–11]. The indifferent ions remain within outer (diffuse) part of the electrical double layer and do not strongly adsorb at the solid particle's wall.

The potential at this surface is called the ζ -potential. IEP of dispersed particles and potential determining ions in a solution have important role to understand the adsorption mechanism of various ionic species onto the dispersed particles [12]. Also, they help for flotation or coagulation in various colloidal dispersions.

When the ζ -potential is low, attraction of suspended particles to each other exceeds repulsion and the particles tend to aggregate. The ζ -potential can be determined from measured electrophoretic mobility and Henry's function, $f(\kappa\alpha)$ value is either 1.5 or 1.0. For the Smoluchowski approximation, $f(\kappa\alpha)$ is 1.5 in aqueous (polar) solutions. For the Hückel approximation, $f(\kappa\alpha)$ is 1.0 in non-polar medium [13–15].

As shown in **Figure 2**, when ζ -potential value of a dispersion is more positive than +30 mV or less negative than -30 mV, the dispersed particles will tend to be stable. Some parameters such as time, pH, ion and surfactant concentrations and types, and temperature may affect the value of ζ -potential [16, 17].

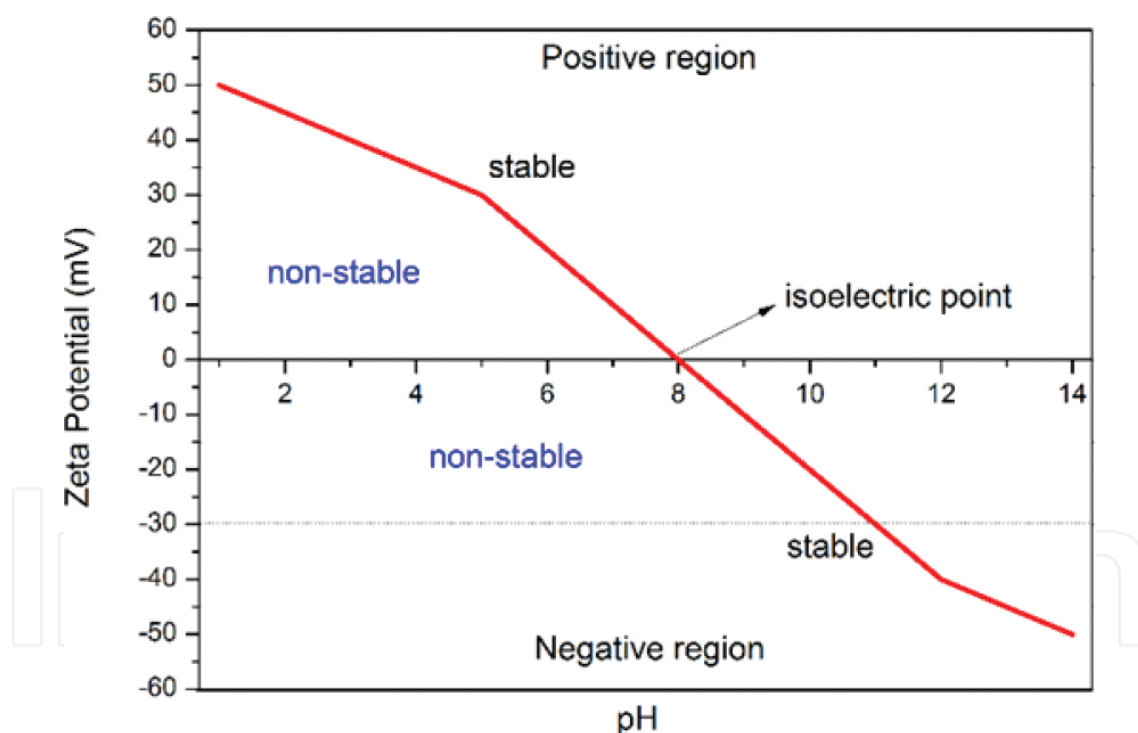


Figure 2. Schematic illustration of change of zeta (ζ) potential with pH.

1.2. Conducting polymers

Conducting polymers have unique properties such as electrical stability, ease of synthesis and durability leading to a variety of potential applications. Conjugated polymers have attracted enormous attentions from both science and technology as semiconductors and electroactive

materials for their applications in batteries, molecular electronic devices, sensors, solid phase extractions and light emitting diodes [18–21]. The most common conducting polymers are polypyrrole, polythiophene and polyaniline, as shown in **Figure 3**. The biggest advantage of these polymers is their processability, mainly by dispersion.

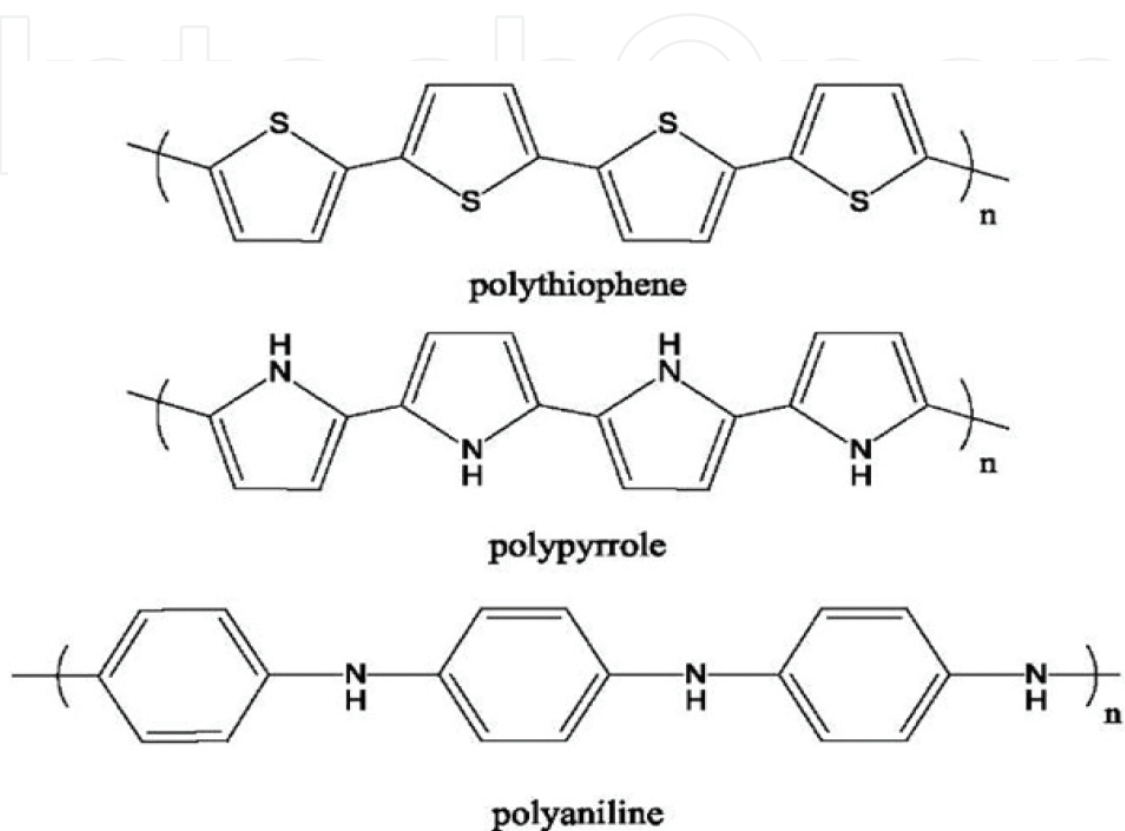


Figure 3. Chemical structures of some conjugated conducting polymers.

1.3. Chitosan as a biodegradable polymer

Polysaccharides are a major class of biomaterials, such as chitosan, chitin, starch, cellulose and alginate. Chitin is extracted from the shells of crustaceans like crabs and shrimps [22]. Chitosan [poly (β -(1-4)-2-amino-2-deoxy-D-glucan)] is *N*-deacetylated derivative of chitin (**Figure 4**). CS is a polycationic and insulating biopolymer and contains free amino groups ($-NH_2$) at neutral and alkaline pH values, but they are protonated ($-NH_3^+$) under acidic conditions, thus making ionic interactions possible upon the reaction with anions [23–26]. CS has interesting characteristics such as biodegradability, chemical inertness, biocompatibility and low cost. Therefore, chemical derivatives of CS with conducting polymers are important topic for production of multi-functional materials. CS as a biodegradable polymer have been using in many application area especially in the food and medical industry. Chitosan is easily enzymatically biodegradable in nature [27].

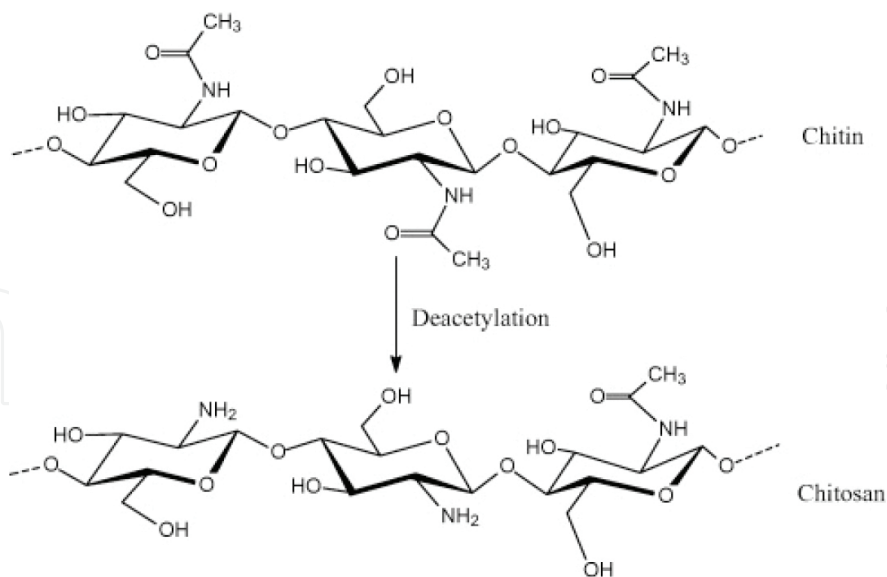


Figure 4. Structures of chitin and chitosan.

2. Electrokinetic measurements of colloidal particles

The incorporation of conducting polymers into natural polymers can enhance the performance of both the 'host' and the 'guest' thereby leading to interesting physical and chemical properties [28]. Generally, fabrication of CP/CS composite is carried out by chemical polymerization of monomer such as aniline, pyrrole and thiophene using as initiator (FeCl_3 , APS, etc.) in the presence of 1% CS solution. The ζ -potential measurements are performed with a Malvern Nano ZS which works with Laser Doppler Electrophoresis technique using folded capillary cell equipped with gold electrodes (**Figure 5**). Note that 0.1 g/L dispersions is taken and pH value is adjusted with 0.1 M $\text{HCl}_{(\text{aq})}$ and 0.1 M $\text{NaOH}_{(\text{aq})}$ solution.



Figure 5. Image of the Malvern Nano Zeta Sizer.

Zeta-Sizer software is used for the ζ -potential measurements of the dispersed particles. In aqueous medium, the ζ -potential is determined by using the Smoluchowski model. The thickness of the electrical double layer, EDL (κ^{-1}) is accepted to be smaller in comparison with the particle size. First, to measure surface potential, solid particles are dispersed in deionized water as 0.1 g/L concentration. This dispersion is subjected to ultrasonication for 30–60 min. And then the dispersion is left to establish equilibrium for 2–3 h. Finally, the supernatant liquid is taken for the ζ -potential measurements. pH of the dispersion is adjusted with diluted $\text{HCl}_{(\text{aq})}$ and $\text{NaOH}_{(\text{aq})}$ solution by MPT-2 autotitrator unit at 25°C. The effects of pH, electrolytes, surfactants and temperature on the ζ -potentials of the colloidal dispersions can be investigated.

2.1. Effect of pH on colloidal behaviour of dispersions

Electrokinetic properties of polyaniline, polypyrrole and polythiophene-chitosan composites are given as a function of pH in **Figure 6**. It is shown that ζ -potential values of the conducting polymers increase and shift to positive region due to positive surface charge of polycationic chitosan molecules in the composite structure. At the same time, it causes to an increase in colloidal stabilities of the dispersed particles. With the addition of $\text{HCl}_{(\text{aq})}$ solution into the dispersion medium, concentration of hydronium cations increases in the aqueous dispersion, and the particle surfaces are surrounded by the hydronium ions. This causes to the protonation of the amino groups of CS or the selective adsorption of the hydronium cations on the surfaces of the dispersed colloidal particles. As a result, the ζ -potential values of the particles gradually increase with decreasing pH values, as shown in **Figure 6**. ζ -potential of CS molecules is related with number of $-\text{NH}_3^+$ ions [29]. With the addition of $\text{NaOH}_{(\text{aq})}$ solution into the dispersion medium, number of hydronium ions reduces and the number of OH^- anions increases. And then, deprotonation of protonated $-\text{NH}_3^+$ ions to $-\text{NH}_2$ and selective adsorption of OH^- anions on the surfaces of the dispersed particles occur. As a result, ζ -potential of the colloidal dispersions decreases and shifts to more negative values due to the overcompensation of the positive surface charge with the negatively charged counter ions.

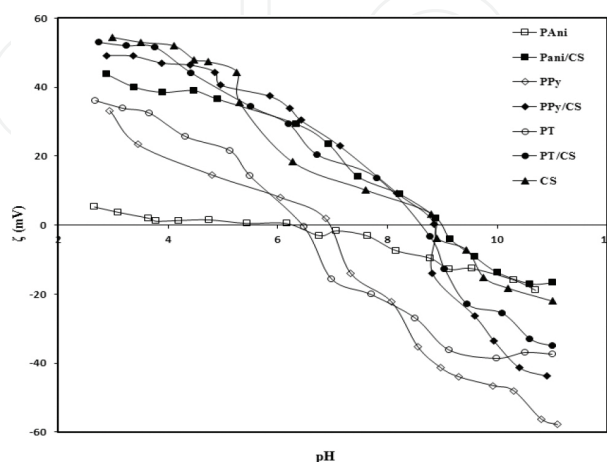


Figure 6. Change of ζ -potential with pH, 10^{-3} M NaCl, $c = 0.1$ g/L, $T = 25^\circ\text{C}$.

Dispersed particles have zero surface charge at their isoelectric points. At this point, number of positive charges is equal to the number of negative charges. Therefore, the particles in a solution are only stabilized by steric effect. CS is deprotonated around pH 8.5 due to the zwitterionic structure of carboxyl groups in CS molecules. To signify the unique zwitterionic properties, the CS derivatives are named as zwitterionic chitosans. Conducting polymers may act as anion or cation exchangers [30–33].

2.2. Effect of electrolytes on colloidal behaviour of dispersions

The effect of cationic and anionic electrolytes on ζ -potentials of conducting polymers and their CS composites is presented in **Figure 7**. As can be seen, monovalent (Na^+) and divalent (Ba^{2+}) cations and divalent (SO_4^{2-}) anions are indifferent ions which only compressed the electrical double layer. As shown in **Figure 7**, ζ -potential values of colloidal particles shift to the positive regions in 1 M BaCl_2 solution due to increasing valency of the cations. It can be attributed to the larger ionic radius of the Ba^{2+} ions, which makes difficult to exchange with the other ions such as Na^+ present in the dispersion. On the other hand, with increasing valency of the anion, ζ -potential of the colloidal dispersions shifts to more negative region. It can be attributed the presence of a Stern layer formed by negatively charged divalent counter ions (SO_4^{2-}), over compensating the positive surface charge of the colloidal particles [34, 35]. Also, it was observed that IEP values of the dispersions shift to higher or lower pH values with increasing ionic strength of the cations and anions present in the dispersion medium, respectively.

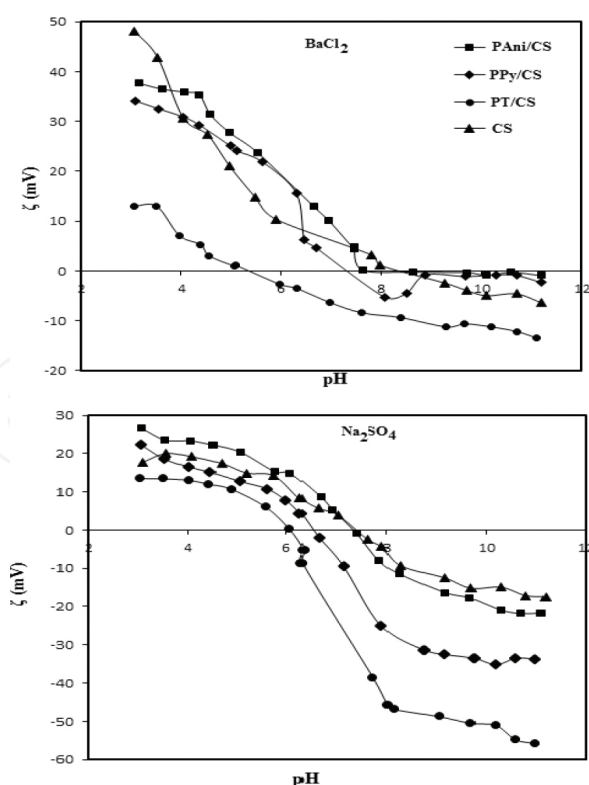


Figure 7. Change of ζ -potential with pH, 10^{-3} M BaCl_2 and Na_2SO_4 , $c = 0.1$ g/L, $T = 25^\circ\text{C}$.

2.3. Effect of various surfactants on the ζ -potential of colloidal dispersions

A small amount of surfactants could be adsorbed easily on the surfaces of the dispersed particles due to their hydrophobic surfaces and cause rapid ζ -potential change. The changes in ζ -potentials of the colloidal dispersions as a function of cationic (CTAB), anionic (SDS) and nonionic (Triton X-100) surfactant concentrations are given in **Figure 8**. As shown, CTAB is added into the colloidal dispersion, ζ -potential of the dispersions increases, without passing through an IEP. After the surface coverage is completed, ζ -potential value slowly decreases and then similarly charged CTAB ions repulsive each other [36, 37]. With the addition of the anionic SDS molecules, the surface coverage of the particles increases with an increasing number of negatively charged SDS molecules. As a result, ζ -potential of the particles in the dispersion shifts to negative values with passing through an IEP. It may be caused by the electrostatic interactions between the negatively charged SDS tails and the positively charged CP/CS surfaces [38]. On the other hand, with the addition of non-ionic surfactant (Triton X-100), ζ -potential value of the colloidal dispersion is almost similar, as shown in **Figure 8**.

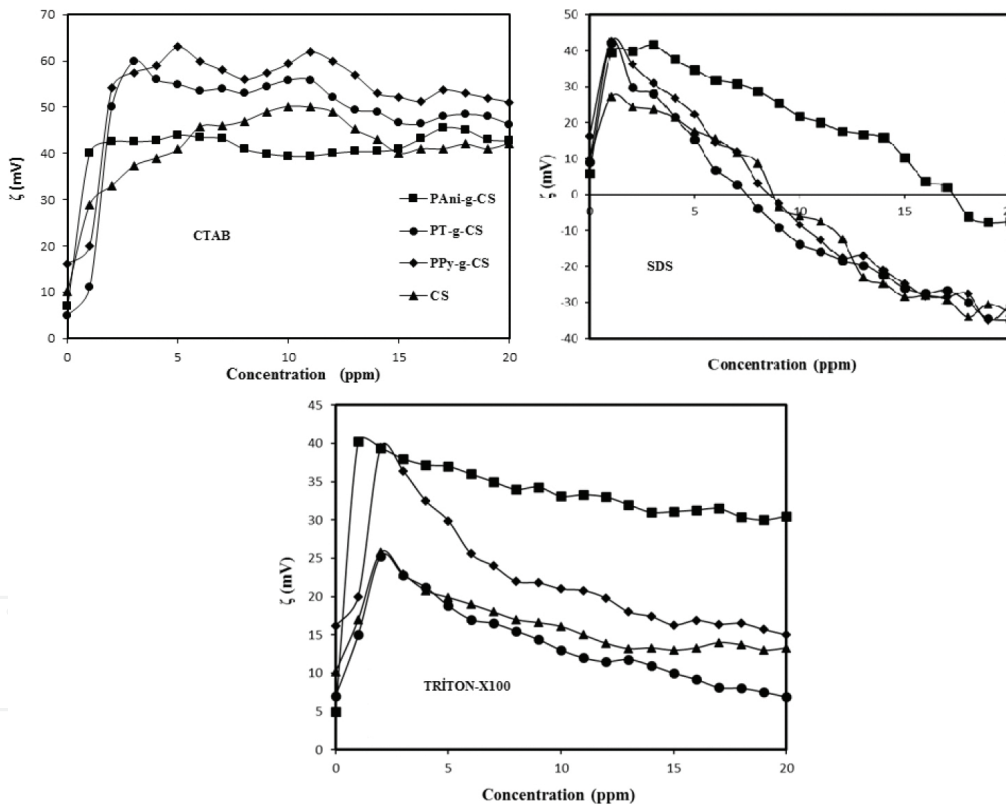


Figure 8. Effect of surfactant type on ζ -potential of colloidal dispersions.

It is known that mobility of the dispersed particles increases with increasing temperature. When the ionic mobility increases, viscosity of dispersion decreases at higher temperatures [39, 40]. Therefore, the establishment of diffuse layer leading to the formation of ζ -potential around the particles becomes difficult. Therefore, ζ -potential value of the CP/CS dispersions decreases with increasing temperature.

3. Conclusion

These results showed that the ζ -potential of the both CP and CS can be changed with the synthesis of their CP/CS composites. Besides, the ζ -potential of CP/CS colloidal dispersions can be altered by using different electrolytes, cationic or anionic surfactants and their colloidal stability can be improved. It is an important result from their industrial applications point of view.

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