

Electrokinetic Potential of Kaolinite Clay in the Presence of Polystyrene Sulfonate

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ABSTRACT: The determination of the electrokinetic potential of clay is very important in many applications. Therefore, this work was aimed at studying the effect of poly(4-sodium styrene sulfonate) on the electrokinetic potential and the sedimentation behavior of kaolinite clays at different pH values and/or in the presence of sodium or calcium chlorides. At pH values lower than the point of zero charge (PZC) of the kaolinite clay, the zeta potential of Na- or Ca-kaolinite in CaCl₂ solutions was higher than that in NaCl solutions at the same concentration. Above the PZC, the zeta potential of Na- or Ca-kaolinite in NaCl solution was higher than that in CaCl₂ at the same electrolyte concentration. These results reflect the ability of calcium cations to compress the double layer of the kaolinite clay better than sodium cations. Also, below the PZC and at low concentra-

tions of poly(4-sodium styrene sulfonate), the zeta potential of the kaolinite clay suspensions had low value, while the sediment volumes had higher values. On the other hand, above the PZC at increasing polymer concentrations, the zeta potentials increased but the sediment volumes had lower values compared to those produced below the PZC. The data showed the zeta potential of Na-kaolinite suspensions are higher than Ca-kaolinite, producing lower sediment volumes of Na-kaolinite compared to Ca-kaolinite at the same concentrations of polymer and/or pHs. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1705–1711, 2006

Key words: kaolinite clay; polystyrene sulfonate; electrokinetic potential; sedimentation

INTRODUCTION

Kaolinite is widely used in the ceramic industry, paper coating, and as filler in paints, rubber, and other plastic materials, as well as a catalyst support. Also, it is of great importance for its action in adhesives applications, lubricants, water clarification, medicine, and different activities in the petroleum field.^{1,2}

Kaolinite has a simple structure with a single layer of tetrahedral coordinated ions linked through oxygen to a layer of aluminum octahedral. The summits of the octahedral are exclusively hydroxyl units. The intermediate anion sites are occupied by both oxygens and hydroxyls. Thus, kaolin is referred to as a 1 : 1 layer structure.³

The measurement of the electrophoretic mobility of colloidal particles in suspension is a key technique for the determination of the surface properties of the particles, usually characterized by the zeta potential (ξ). In an electric field, suspended particles will migrate at mobility proportional to their surface charge and the applied field strength. The applied electric field convicts the charged fluid in the double layer around the

particle, causing electrophoretic migration in the opposite direction; since the combination is electrically neutral, there is no net force on the particle and its double layer. In a heterogeneous suspension, particles with different surface charges will have different electrophoretic mobility, leading to the possibility that they will colloid and aggregate.^{4,5}

Simple inorganic electrolytes can have a significant impact on the zeta potential. The effect depends on the relative valence of the ions and on their concentration. Also the electrokinetic potential of the kaolinite clay is greatly affected by the adsorbed polymer molecules, which are firmly attached to the clay surface due to their ability to form multiple adsorption bonds. These adsorbed polymers have a considerable thickness, giving rise to an interfacial zone with special properties. To gain insight into this phenomenon and in the factors affecting them, much work is necessary, especially on kaolinite.^{6–8}

The objective of this article was to investigate the effect of anionic poly(4-sodium styrene sulfonate) adsorption on the zeta potential and the sedimentation behavior of kaolinite clays at different pHs. The effect of sodium and calcium chlorides on ξ of kaolinite clay will be also investigated.

TABLE I
Cation Exchange Capacity (CEC) and Surface Area of Kaolinite Clay Samples

	Sample A ^a		Sample B ^b		Sample C ^c	
	Ca	Na	Ca	Na	Ca	Na
CEC (mEq/100 g)	7.98	7.40	12.20	11.52	20.90	21.50
Surface area (m ² /g)	10.3064		12.1621		13.5665	

^a Bed Selected.

^b New Esila.

^c Kalabsha.

EXPERIMENTAL

Three Egyptian kaolinite samples: Bed Selected, New Esila (from Sinai), and Kalabsha (from Aswan) were the candidates of this study. The three types of kaolinite samples are denoted A, B, and C, respectively. The clay was washed and particle sizes less than 20 μm were separated.⁹ The homoionic surface kaolinite was obtained by saturating it with sodium or calcium cation.¹⁰

The polymer used was poly(4-sodium styrene sulfonate) from the Sigma-Aldrich Co. and had a molecular weight of 70,000 g mol^{-1} .

The cation exchange capacity (CEC) and the specific surface area of the three kaolinites were recorded in previous work by the authors.¹¹ The physical properties of these kaolinites are given in Table I.

Different experiments were designed to study the zeta potential of kaolinite suspensions under the following conditions:

1. Na- or Ca-kaolinite (0.2% wt/vol) clay suspensions was investigated at different pH values (from 3 to 9).
2. Different concentrations of NaCl or CaCl₂, ranging from 10⁻⁴ to 10⁻² M, were added to the clay at different pH values (from 3 to 9).
3. Different concentrations of poly(4-sodium styrene sulfonate) ranging from 20 to 1000 ppm were added to the kaolinite clay at pH values 3, 6, and 9 \pm 0.15.

The zeta potential of the kaolinite particles was determined using a micro-electrophoresis apparatus (Zeta Meter Inc., USA) using a cylindrical cell.¹²

The sedimentation volumes of sodium or calcium kaolinite clays were measured¹³ with different polymer concentrations ranging from 500 to 2500 ppm at pH 3, 6, and 9 \pm 0.15.

RESULTS AND DISCUSSION

Effect of pH and electrolytes on the zeta potential of kaolinite

Figures 1 and 2 represent the effect of pH (in the range 3 to 9) on the ξ of 2% Na- or Ca-kaolinite suspension

in the presence of NaCl or CaCl₂ with concentrations 10⁻², 10⁻³, and 10⁻⁴ M. The point of zero charge (PZC) was taken at the pH at which ξ curves intersect each other obtained in the presence of different salt concentrations. The PZC of these kaolinite samples are given in Table II. These values are close to those reported by some authors.¹⁴

To investigate the effect of electrolyte on ξ of kaolinite, NaCl or CaCl₂ solutions were used, as shown in Figures 1 and 2. The effect of salt concentration on ξ of kaolinite particles was found to be dependent on pH. At pH values below PZC, an increase in salt concentration led to a decrease in the negative values of ξ . These observations could be due to the double layer compression on both the edges and the faces. At pH values above PZC this behavior reversed, where kaolinite surface carries net negative charges.¹⁵⁻¹⁷

In conclusion, these results reflect the effect of electrolytes on the spatial distribution of the electrical potential and the counter ion charge, in which the degree of compression of the double layer is governed by the concentration and valence of the ions that have the opposite sign as that on the surface charge, whereas the effect of ions of the same sign is comparatively small. Thus, as concentrations as well as the valence of the ions of opposite sign increase, the double layer becomes more compressed.

Effect of polymer adsorption on the zeta potential of kaolinite

The zeta potentials of kaolinite at different polystyrene sulfonate concentrations under different pH values are given in Figure 3. The data revealed that, at low polymer concentrations, up to 100 ppm polymer, the ξ of Na- or Ca- kaolinite suspension has low values, due to partial polymer adsorption. This leads to semi-clay surface covering by polymer adsorption, enhancing the bridging mechanism. As polymer concentration increased, the ξ increased at certain pH values, due to the increase in clay surface covering by polymer adsorption, leading to a decrease in the chance of bridge formation between clay particles.

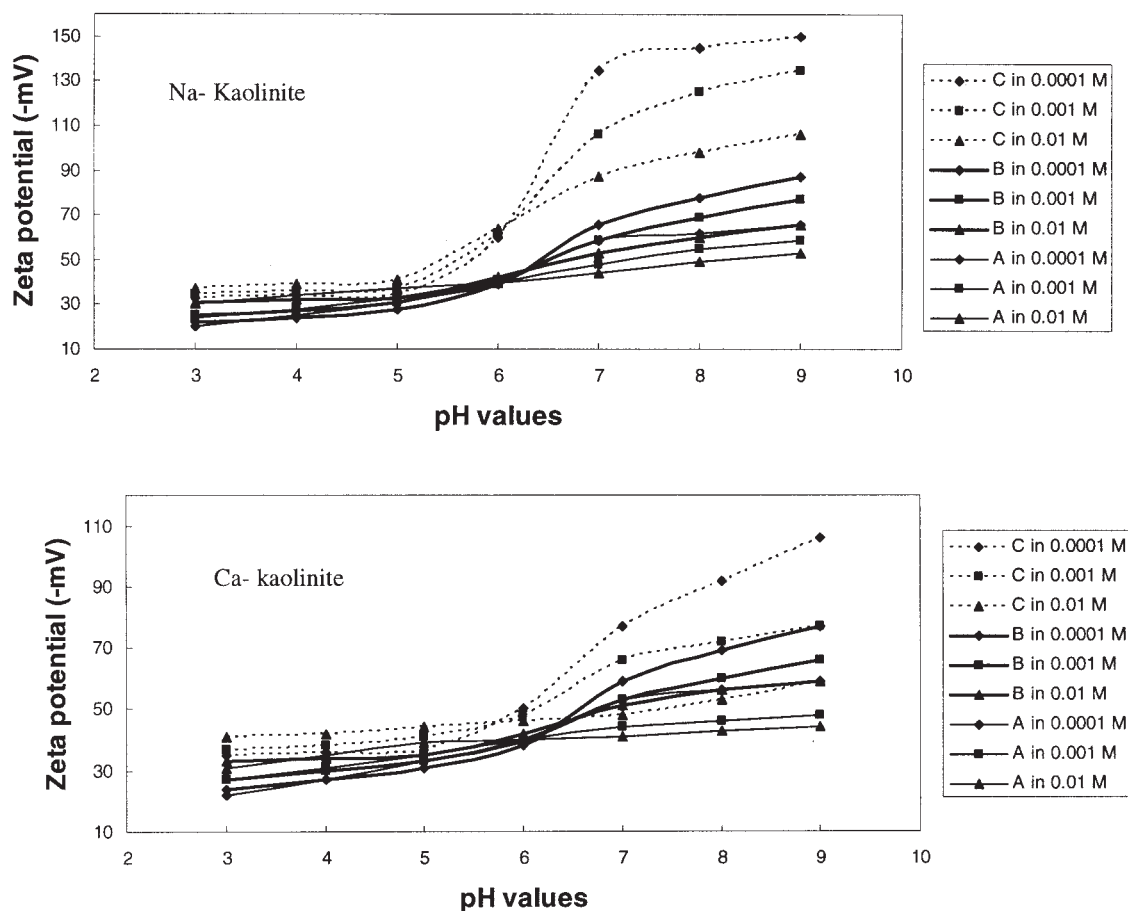


Figure 1 Zeta potential of kaolinite clay suspension in different concentrations of NaCl at different pH values.

It was observed that the magnitude of ξ has the following order regardless of the surface cations; Kalabsha \gg New Esila $>$ Bed selected kaolinite. The higher value of ξ of the Kalabsha kaolinite is due to its higher value of CEC and surface area,^{18,19} as shown in Table I.

Also, as indicated in Figure 3, it was observed that the ξ of Na-kaolinite was generally higher than that of Ca-kaolinite at the same pH. This is due to the divalence of calcium ions, which makes the double layer much more compressed and attracted to each other than that in the case of monovalent ions such as the sodium ion. Divalent calcium ions may affect the anionic polymer kaolinite system in the following ways: (i) by compressing the thickness of the double layer of the kaolinite particles, thereby reducing interparticle repulsive forces, (ii) by reducing the repulsive forces between the anionic polymer and kaolinite particles, and (iii) by reducing interaction between polymer molecules adsorbed on the kaolinite surface. Therefore the clay particles are closer to each other, so the ξ of Ca-kaolinite suspension in presence of the adsorbed anionic polymer is much lower compared to the Na-kaolinite system.^{20,21}

The ξ of Na- or Ca-kaolinite suspension at pH values below PZC is low compared with that at pH values above PZC at the same polymer concentration. This could be explained according to the surface potential at the edges of kaolinite clay, which is a function of pH. These edges become negatively charged due to the interaction of edged ions with the potential determining ions, especially above the PZC. Contrary to that, the basal surfaces are considered to be independent of the pH, which always has negative charges. So, at pH values lower than PZC, the edges become positively charged. Therefore an electrical interaction is promoted between these edge faces and the negatively charged polymer chains adsorbed on the basal surface. This leads to reduction in the repulsive forces between the clay particles; consequently, the ξ of Na- or Ca-kaolinite suspensions have low values. While at pH values above PZC, both the edges and basal surfaces are negatively charged, then the repulsive forces between the basal surfaces and the edge surfaces are common, and consequently ξ of Na- or Ca-kaolinite is higher than that at low pH.²² Therefore sorption of the anionic polymer onto kaolinite surface in-

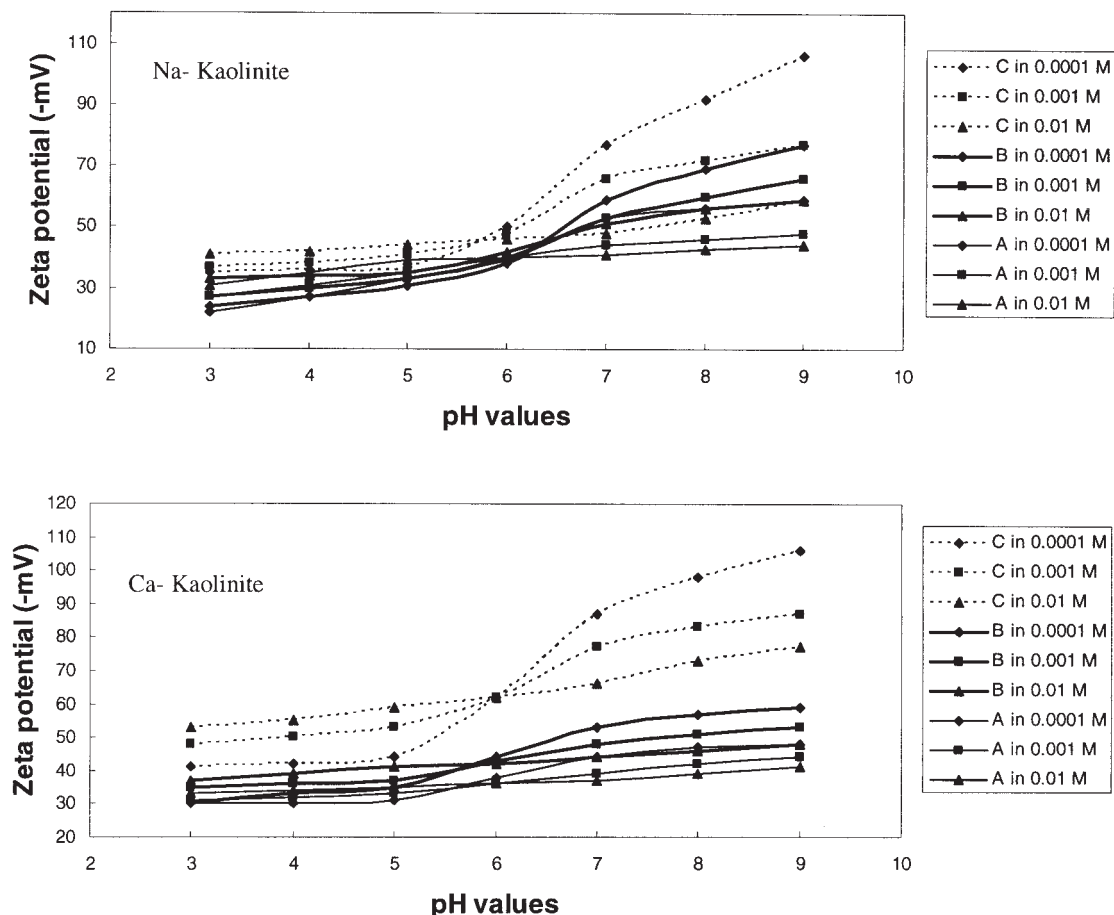


Figure 2 Zeta potential of kaolinite clay suspension in different concentrations of CaCl_2 at different pH values.

duces kaolinite stability due to the repulsion between particles and the polymer negative chain.^{23,24}

Influence of pH and polymer adsorption on sedimentation behavior of kaolinite

The sedimentation volumes of 5% Na- or Ca-kaolinite suspensions in the presence of different polymer concentrations and pH after aging for 7 days are shown in Figure 4 and Table III. The results showed that, at zero polymer concentration, the

sediment volumes of the kaolinite suspensions at pH values below PZC were higher than that of the others at pH values above PZC. These results could be explained according to the clay structure and the electrical property of edges and faces of kaolinite particles. Since kaolinite particles have a platelike shape, in aqueous suspensions, particles can be associated in three basic modes: edge to edge (EE), edge to face (EF), and face to face (FF), depending on the pH of the kaolinite suspension. The electrical interaction energy for these three types of association is governed by three different combinations of the double layers. Also, the rate of diffusion of the particles as they approach each other in these three ways is the same, and they may not occur simultaneously or to the same extent when the clay suspension is flocculated. For pH values near PZC, the electrical double layer of the clay particles becomes very thin. In our case, this was close to pH 6, FF domains can form more easily in the sedimentation process. This refers to the collapse of the diffuse double layers and the formation of aggregates of parallel plates with small space between them. This type of aggregate produces sediment volume inter-

TABLE II

Point of Zero Charge (PZC) of Kaolinite Clay Samples

Kaolinite sample		PZC
Na	A	6.8
	B	6.24
	C	6.12
Ca	A	5.60
	B	5.60
	C	6.00

^a Bed Selected.

^b New Esila.

^c Kalabsha.

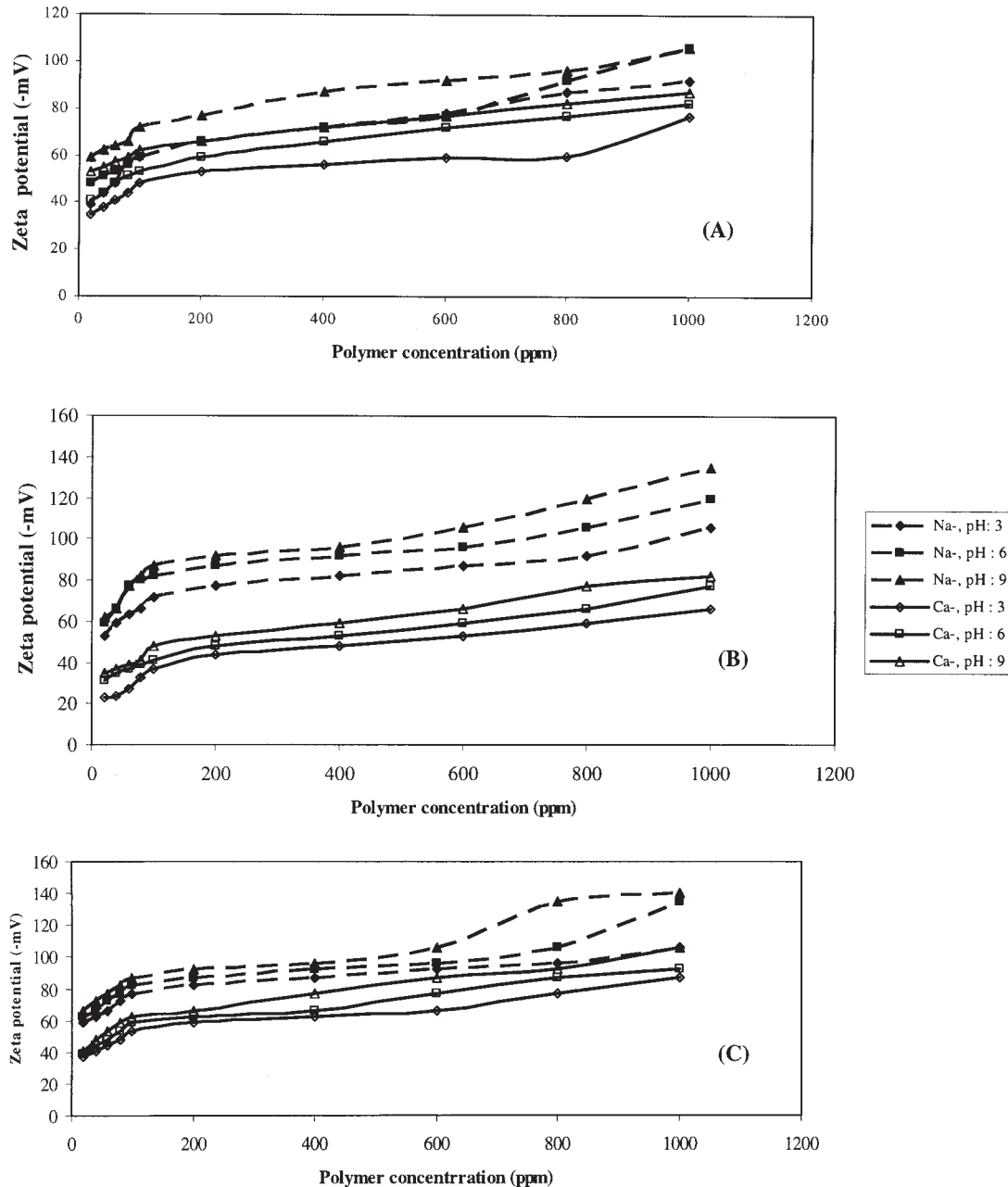


Figure 3 Zeta potential of Na- and Ca-kaolinite suspension in different concentrations of polystyrene sulfonate at different pH values; (A) Bed Selected, (B) New Esila, and (C) Kalabsha.

mediate between EE and EF modes. As discussed above, negatively charged basal surfaces of the kaolinite plates were pH independent and the edges charges were pH dependent, therefore EF association is favorable below PZC. Above PZC, the kaolinite particles were connected in EE mode.²⁵

Also, it was found that, as polymer concentration increased, the sediment volumes of kaolinite suspension decreased at the same pH. The variation in sediment volumes of kaolinite clays fluctuated by polymer concentrations. This was attributed to the adsorption of the negative chain of the anionic polymer, which

leads to an increase in the electrical repulsion of identically negative charged double layers around kaolinite particles and consequently the chance of EF, EE, and FF contacts being minimized, and the kaolinite system remains dispersed.^{26,27} Therefore the sediment volume of Na- or Ca-kaolinite suspension is decreased with increased polymer adsorption.

The structure of the double layer kaolinite is largely affected by the nature of the exchangeable cation and the hydration energy of such cations; the sediment volumes of Ca- kaolinite gave higher values than Na-kaolinite at the same pH values and polymer concen-

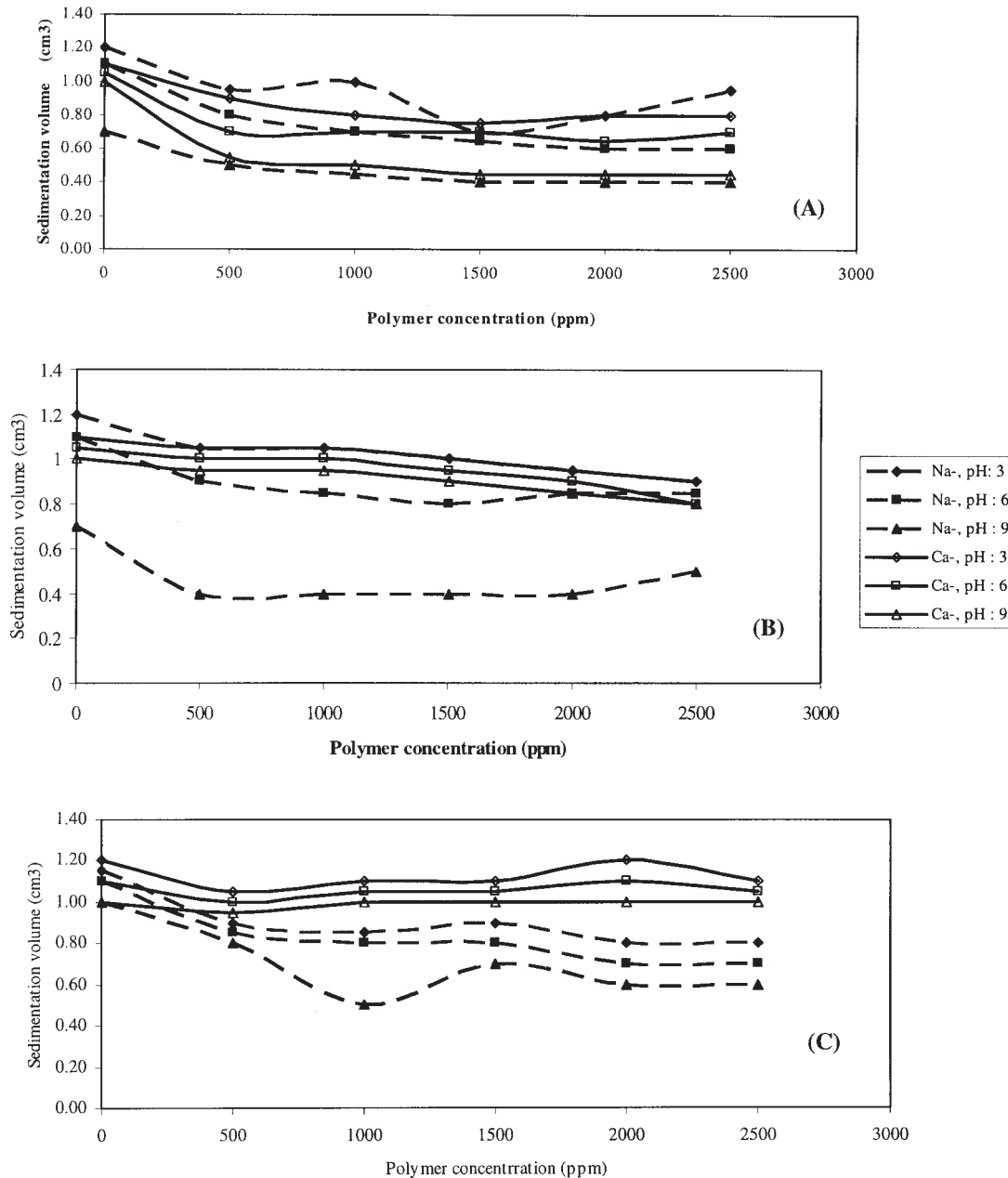


Figure 4 Sedimentation volume of Na- and Ca-kaolinite suspension in different concentrations of polystyrene sulfonate at different pH values: (A) Bed Selected, (B) New Esila, and (C) Kalabsha.

trations. This could be explained through the effect of the exchangeable cations. The calcium as a divalent cation has to have more coagulation power than that of the sodium ions.^{28,29} The stability of the colloidal system can often be explained by the classic DLVO theory. This theory explains the interaction energy between two similarly charged colloidal particles, which is determined by the sum of the electrostatic repulsive energy and attractive forces arising from van der Waals interactions.³⁰ The magnitude of electrostatic repulsive forces between two particles is a function of the distance of four parameters: separation,

TABLE III
Sediment Volumes of Kaolinite Clay Samples at Different pH Values After Aging 7 Days

Kaolinite clay samples		Sediment volumes (cm ³)		
		pH 3	pH 6	pH 9
Na	A	1.20	1.10	0.70
	B	1.20	1.10	0.70
	C	1.15	1.10	1.00
Ca	A	1.10	1.05	1.00
	B	1.10	1.05	1.00
	C	1.20	1.10	1.00

^a Bed Selected.
^b New Esila.
^c Kalabsha.

valence, concentration of counter ions, and the net total surface charge density. The negative polymer could be adsorbed on negatively charged suspensions through a bridging concept in which long polymer loops interconnect one particle to another and adsorb thereon through bridging. The loops should be longer than the thickness of the double layer to obtain effective flocculation. Additional repulsive forces due to adsorbed anionic polymer can also affect the flocculation of particles. The results of this work indicate that the sorption of polystyrene sulfonate onto kaolinite increases suspension stability due to the repulsion between the particles and polymer chains (electrostatic stabilization).³¹

Another mechanism by which polystyrene sulfonate increases colloid stability is steric stabilization caused by a thermodynamic repulsion that occurs between interpenetrating polymer chains attached to the colloid surfaces, which is in agreement with the above concepts.³²

CONCLUSIONS

- High stability of kaolinite colloidal systems was obtained above the PZC, where the surface charges have a mutually repelling action.
- The adsorption of polystyrene sulfonate onto the kaolinite surface increased the stability of kaolinite suspensions above the PZC.
- The mode of kaolinite particles settling depends on the pH of the medium and polystyrene sulfonate concentrations.

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