

# Difference in the Influence of Na and Ca Ions on the Zeta Potentials of Anatolian Bentonitic Clays

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**Abstract.** The values of the zeta potentials for bentonitic clay particles suspended in solutions of NaCl,  $(\text{NaPO}_3)_n$  and  $\text{CaCl}_2$  at different electrolyte concentrations and constant pH ( $\sim 7$ ) were measured. When Ca salts were added to the clay solutions in increasing concentrations, the double layers of particle surfaces gradually contract, become narrower and the zeta potential value decreases. When Na salts were used, the zeta potential increased with increasing concentration.

**Key words:** Bentonitic clays; electrokinetics, zeta potential, exchangeable cations.

## 1. Introduction

Today, zeta potential measurements are used especially in medicine, in biomedical determinations, and in metallurgy for the determination of the flocculent nature of the media used in floatation of mineral oxides [1, 2]. There are many related studies which are based on the microelectrophoretic behaviour of colloidal suspensions other than clay–water systems [3–5]. Clay–water systems are generally more complex.

Bentonitic clay, with a large amount of montmorillonite mineral, shows a colloidal structure because of its internal structure and the small particle size. However, owing to the particle structure, shape, charge distribution, and ion exchangeability, the behaviour of colloidal bentonitic clay suspensions is much more difficult to interpret and predict than that of most other clay soils [6–8]. Bentonite tactoids constitute the solid particles in polar liquids. Their other important characteristics are the presence of exchangeable cations with opposite charges from the ones on the surface and the possible simultaneous presence of positive charges within fractures at the edges of clay particles. Such properties lead to discrepancies among the results of rheological experiments and make their interpretation difficult [6, 7]. The interesting behaviour of montmorillonite clay must also not be forgotten when

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Table I. Structural formulas of the samples.

Sample	
Kurşunlu	$(\text{Si}_{7.181}\text{Al}_{0.819})\text{O}_{20}(\text{Al}_{1.1016}\text{Fe}_{0.2664}\text{Mg}_{0.3277}\text{Ti}_{0.285})(\text{Ca}_{1.0686}\text{K}_{1.1684}\text{Na}_{0.6492})(\text{OH})_4$
Sarıcaaya	$(\text{Si}_{6.3728}\text{Al}_{1.6272})\text{O}_{20}(\text{Al}_{0.1312}\text{Fe}_{0.3442}\text{Mg}_{0.2451}\text{Ti}_{0.069})(\text{Ca}_{0.3380}\text{K}_{0.3723}\text{Na}_{0.2868})(\text{OH})_4$
Ünye	$(\text{Si}_{7.7252}\text{Al}_{0.2748})\text{O}_{20}(\text{Al}_{1.6664}\text{Fe}_{0.0898}\text{Mg}_{0.3764}\text{Ti}_{0.02476})(\text{Ca}_{0.3764}\text{K}_{0.7858}\text{Na}_{0.7528})(\text{OH})_4$

the experimental data are being interpreted. There is great difficulty, too, in the interpretation of the data on the zeta potential, which is a measure of the magnitude and extent of the forces arising as a result of the electrical charges on a particle [9].

In studies carried out with the purpose of determining the surface properties of the clay particles in clay suspensions, cation adsorption, electrophoresis and solution stabilities generally were emphasized, and the zeta potential measurements were performed as a function of pH and the concentration of the electrolyte used [3–5].

Publications related to the calculation of surface charge densities of montmorillonite particles in different liquid media by using zeta potential data are present in the literature [5]. The variation of the zeta potential values as a function of the type of interstitial, exchangeable cations present in montmorillonites has also been reported [4, 5, 10–12]. These studies have indicated that the most important factors which influence both the zeta potential values and the surface charge on the particles are the value of the charge on the cation present in the salt and the pH of the medium.

The purpose of this study is to interpret the effects of the type of bentonite, the type of electrolyte and the electrolyte concentration on zeta potential values. It is also intended to reveal the behavioral differences in the influence of Na and Ca ions on the zeta potentials of three different bentonitic clays which vary in composition and are obtained from three important sources in Turkey. There are numerous sources of bentonite clays in our country. However, in their present condition they have no commercial value. Their qualities would be improved by the addition of electrolytes. In order to improve the quality of these bentonites, in order to achieve widespread use, it is extremely important to know the effects of various electrolytes on the stabilities of bentonite clays.

## 2. Experimental

Ore samples taken from Kuragunlu, Sarıcakaya and Ünye sites have been identified as bentonitic clay minerals using XRD, DTA-TG and IR analysis methods [13–16]. A weighed amount of the samples was kept in an oven until they reached constant weight, and then sieved through 45  $\mu\text{m}$ . Chemical analyses were performed using a Perkin Elmer 3030 Model atomic absorption spectrophotometer. The structural formulas are shown in Table I.

The percentage exchangeable cation of the samples used in this study have been determined using a Flammen Photometer. The percentage Ca of the Kurşunlu sample is the highest, while the Unye sample contains the highest percentage Na. In the Sarıcakaya sample the Ca and Na contents are nearly equal.

Zeta potential measurements were carried out using a zeta meter 3.0 (Zetameter Inc., USA), a microelectrophoresis instrument equipped with microprocessing. The measured electrophoretic mobilities are automatically converted into zeta potentials by means of a built-in microprocessor. The microprocessor basically uses the Smoluchoski equation. The maximum ionic strength used in all measurements was below 0.1 M which corresponds to a double layer thickness ( $1/K$ ) of about 10 Å. Since the particle sizes used for the measurement of zeta potentials are a few micrometers, and the solubility of cations in clay minerals is over  $10^{-3}$  M, the condition of  $Ka \gg 1$  is obeyed under almost all conditions and the Smoluchoski equation is valid. In addition, the range of zeta potentials obtained in this study generally remains below 25 mV. This effect minimizes retardation and relaxation effects and the overall error stays within an acceptable range [17]. 100 mg Samples sieved through 325 mesh sieves were stirred in 100 mL solutions (NaCl, CaCl<sub>2</sub>, or (NaPO<sub>3</sub>)<sub>n</sub>) for 10 min using a magnetic stirrer, and left to stand for 5 min. During each measurement, the motions of a minimum of 20 particles were followed and the average zeta potential value was determined. All measurements were made at ambient temperature (22–26 °C) and converted to 25 °C by the correction factors provided in the instruction manual. The zeta potential values determined for solutions with various concentrations are given in Figures 1–3.

### 3. Results and Discussions

The zeta potential values (mV) measured in distilled water, are given below in increasing order for the three samples:

1. Kurşunlu (with excess Ca) 4.42 ±
2. Sarıcakaya (with approximately equal amounts of Ca and Na) 7.61 ±
3. Unye (with excess Na) 8.30 ±

As indicated by the order of zeta potential values above, the presence of increasing amounts of Na in the bentonite as an exchangeable cation causes an increase in the zeta potential of the bentonite. This is an expected result. The sodium cation has high mobility and interacts loosely with the bentonite layers. The Na ion is easily detached from the surface of the particle upon contact with water (Figure 4). Thus, the potential difference between the relatively more negative particle surface and the liquid phase increases, which results in an increased zeta potential value [6, 7]. In addition the dilation capacity in water of Na-containing bentonites is high. The dilation increases the particle surface and, as a result, increases the adsorption capacity for oppositely charged ions. Since this situation would also cause

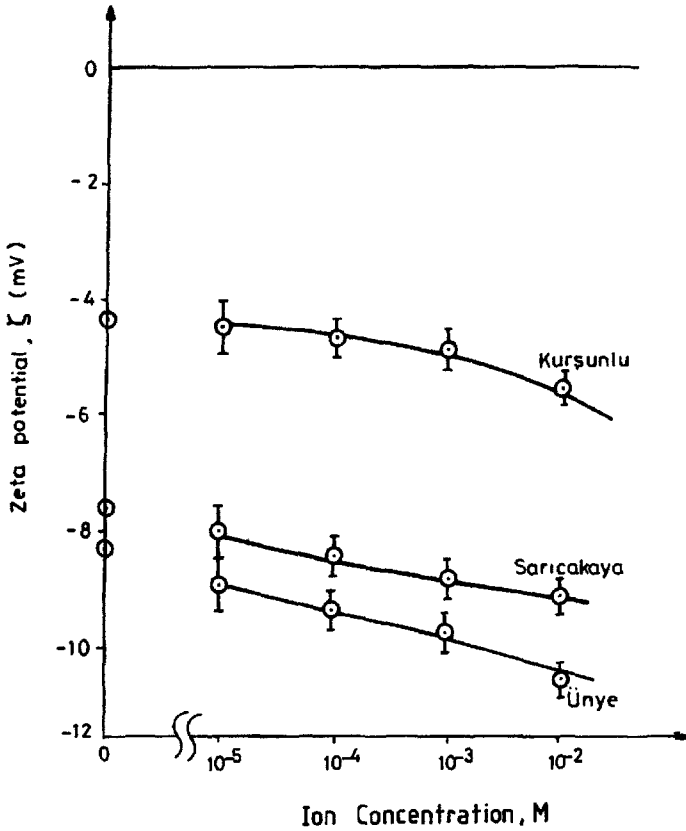


Figure 1. Zeta potential of samples as a function of NaCl concentration.

an increase in the potential difference between the liquid phase and the surface, it would result in a high zeta potential value [6, 7, 18–20].

This mechanism works in just the opposite way in the case of the bentonite from Kurşunlu, which contains relatively higher amounts of Ca. The  $\text{Ca}^{2+}$  ions which are more tightly bound to the surface, cause a decrease in the negative character of the surface, and, consequently, since the dilation would be less, the surface area remains small. As a result, the potential difference between the liquid phase and the surface is diminished and the zeta potential value is low. The zeta potential of the sample from Kurşunlu (Ca-bentonite) is nearly half of the zeta potential of the Ünye sample (Na-bentonite).

When the solid particle is treated with an electrolyte at low concentrations, the expected outcome is a gradual increase in zeta potential up to a certain value, beyond which the zeta potential should decrease with increasing electrolyte concentration [6, 20]. Because it is well known that solid particles, when suspended in polar liquids, are charged at the surface and move randomly in the dispersion medium. This Brownian motion causes particle–particle collisions. If the attractive van der

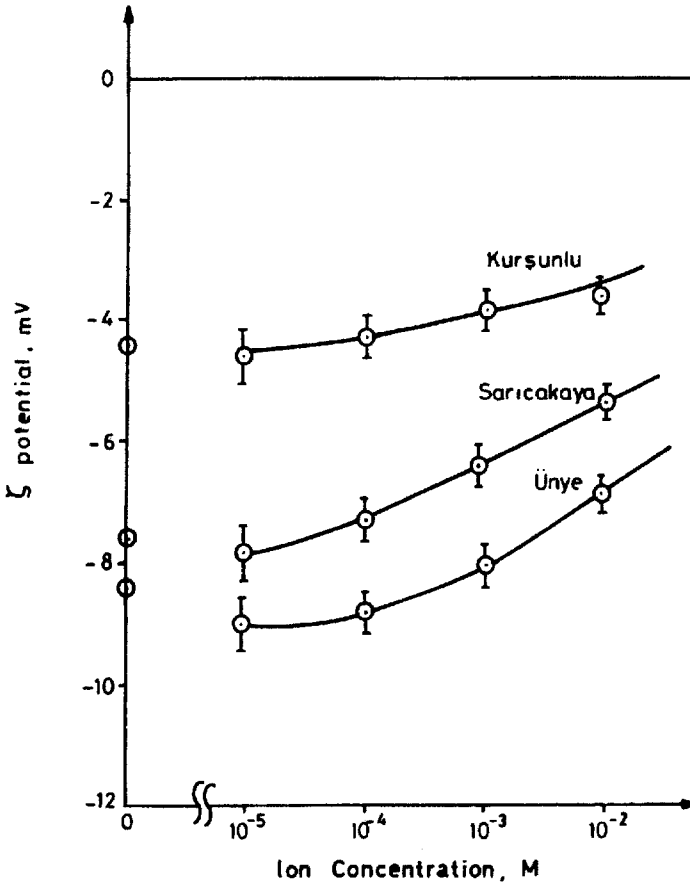


Figure 2. Zeta potential of samples as a function of  $\text{CaCl}_2$  concentration.

Waals forces dominate, the dispersion flocculates. To achieve stable dispersions the repulsive forces must exceed the attractive forces. The repulsive forces are caused by electrostatic interaction between the particles. As the charged particle surfaces absorb more oppositely charged ions upon addition of electrolyte, the repulsive forces greatly exceed the attractive forces, and the zeta potential will increase. This phenomenon occurs at low electrolyte concentration. The increase in zeta potential would be limited when maximum adsorption of the potential-determining ion on the particle surface is reached. Further addition of the electrolyte only increases the charge in the liquid phase and reduces the potential difference between the surface and the liquid. The reduction in surface potential leads to a corresponding reduction in the zeta potential [21]. There are variations in this behaviour of bentonite–electrolyte systems, depending on the type of electrolyte. These variations are caused by the presence of interstitial, exchangeable cations in bentonite granules that form the solid particles and by the simultaneous presence of negative surface charges along with positive charges at fractured edges. Another

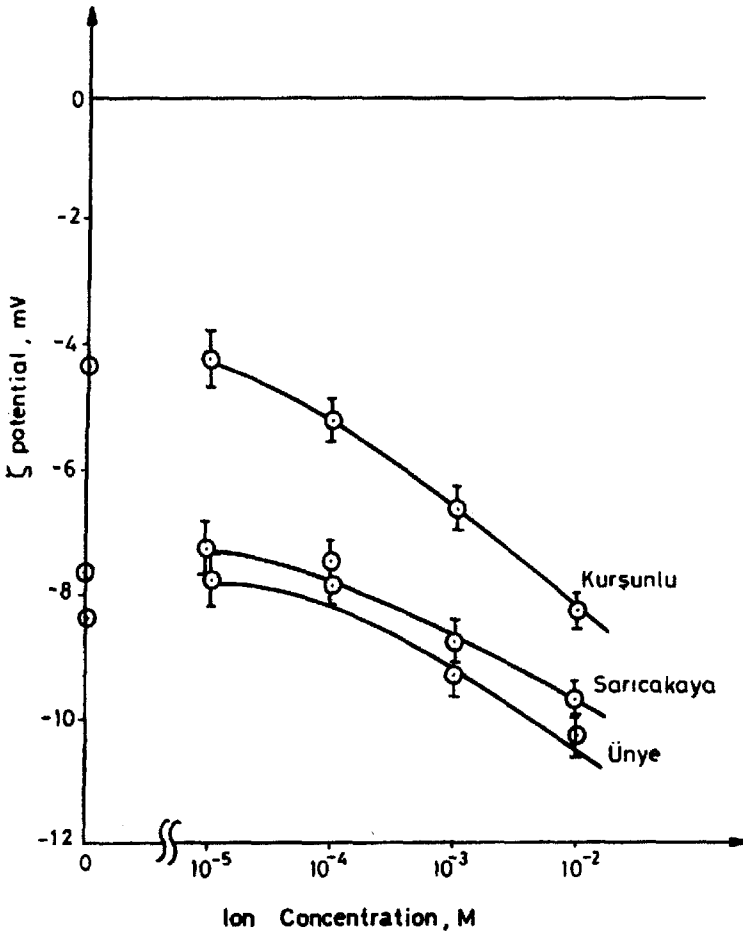


Figure 3. Zeta potential of samples as a function of  $(\text{NaPO}_3)_n$  concentration.

cause of variations in experimental results is the irregular and random shape of bentonite granules, which is far from being a regular, spherical form. Similar to bentonite–water systems, the numerical value of the zeta potential of bentonite–electrolyte systems is closely related to the type of exchangeable cations present in the bentonite (Figures 1–3). Even though the variation in zeta potential as a function of electrolyte concentration is closely dependent upon the type of electrolyte; it is independent of the type of exchangeable cation in the bentonite. As observed in Figures 1–3, the behaviour of the zeta potential as a function of concentration is the same with the same electrolyte in all three bentonite samples which differ from each other only in the type of exchangeable cations.

As mentioned above, the important factor is the kind of cation present in the electrolyte. When NaCl is added to bentonites, an increase in zeta potential with increasing concentration of electrolyte is observed (Figure 1); whereas, if  $\text{CaCl}_2$  is

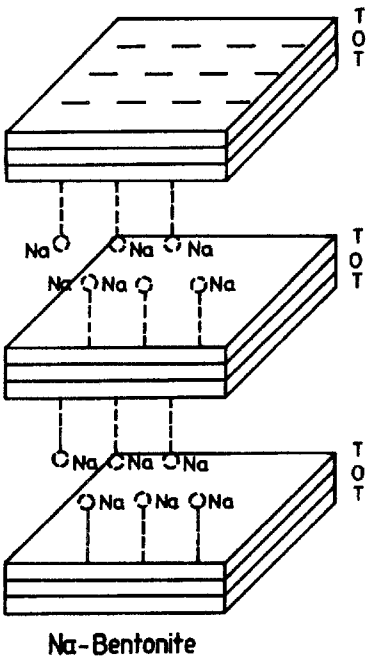
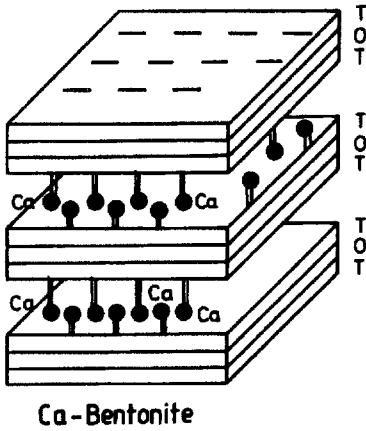


Figure 4. Schematic structure of Ca- and Na-bentonite.

used, the zeta potential decreases with increasing concentrations of this electrolyte (Figure 3). Even if the anions of two electrolytes are the same (Cl), the dependence of the zeta potential on concentration may be reversed if the cations are different. The question why the zeta potential of bentonite–electrolyte systems increases in the presence of Na salts and decreases when Ca-salts are used cannot be answered

at present. When the cation in the electrolyte is Na, the concentration of Na ions around the bentonite particles is expected to increase. When this happens, it is likely that the Na ions, which have high mobility, would be exchanged for higher positively charged Ca, Al and similar ions present near the edges of the bentonite particles [18–20]. The replacement of these highly charged ions with sodium ions which bear a relatively smaller positive charge, decreases the density of positive charge on the surface of the particles; the surface thus acquires a more negative character [18–20]. As a result, the potential difference between the surface and the liquid phase increases as a function of increasing electrolyte concentration which is observed as a continuous increase in the zeta potential. The same results can be shown in Figures 1 and 2, obtained using our experimental results.

In addition, as a natural consequence of increasing electrolyte concentration, which means a higher concentration of Na cations in the medium, the concentration of interstitial, exchangeable Na cations is expected to increase. Such an increase in the concentration of interstitial Na cations would result in an increase in interlayer distances by dilation of the particles. The larger surface areas of enlarged particles would enhance the adsorption of the oppositely charged ions around the surface; this would result in an increased surface–liquid phase potential difference and increase the zeta potential values (Figures 1 and 2).

These mechanisms are the same as those responsible for the zeta potential of bentonite–water systems. The negatively charged area of the basal plane in a particle might increase with increasing the concentration of  $\text{Na}^+$  ions in the interlayer and/or bulk water phase as a result of the dilation of layers in water, while divalent  $\text{Ca}^{2+}$  ions could bridge two layers, resulting in the increase of the positively charged edge area in a particle. This mechanism is shown in Figure 4. Moreover  $\text{Ca}^{2+}$  ions neutralize the lattice charge of the basal plane of 2:1-type layer silicates more effectively than  $\text{Na}^+$  ions [15].

On the other hand, the anions also have a certain effect on the zeta potential value as observed with electrolytes which contain different anions but the same cation. In this respect, the effects of NaCl and Na metaphosphate on the zeta potential values of bentonites have been investigated (Figures 1 and 2). Due to the presence of Na cations, an increase in zeta potential as a function of increasing electrolyte concentration has been observed with both electrolytes. This may be explained by the relatively greater activity of the phosphate anion, which makes it more effective in neutralizing the positive charges on the surface, resulting in an increase in the density of negative charge at the surface. The increase in density of negative charge on the surface results in a greater potential difference between the surface and the liquid phase which, in turn, increases the zeta potential value. The presence of phosphate ion thus accentuates the effect of Na electrolytes on the zeta potentials of the bentonite–electrolyte systems.



#### 4. Conclusion

The zeta potential of bentonite is a function of the type and concentration of exchangeable cations, of the type of anion and the cation in the electrolyte and of the concentration of the electrolyte.

A more effective increase in zeta potential is obtained with increasing concentrations of Na-containing electrolytes which have relatively more active anions.

The presence of Na cations in the bentonite results in larger zeta potential values. When electrolytes are added, if the cation in the electrolyte is Na, the zeta potential increases for concentration values between  $10^{-2}$ – $10^{-5}$  M. If the cation in the electrolyte is Ca, for the same concentration values a decrease in zeta potential is observed.

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