

## Electrokinetic Potential and Surface Charge Density Relationship of Ca-Bentonite Suspensions in Presence of Mono and Divalent Electrolytes

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**I**N THIS WORK, the distribution of electrokinetic potential and the diffuse particle charge (DPC) in the double layer of Ca-Bentonite towards some electrolytes  $\text{CaCl}_2$  and/or  $\text{NaCl}$  were examined. Also the effects of absolute and equivalent fraction concentrations of these electrolytes on the electrokinetic properties of Ca-Bentonite were studied. The results revealed that at low monovalent cation ( $\text{NaCl}$ ) concentration; 0.01 M/L; the charges increased as  $\text{Na}^+$  ions expand the double layer and to be more diffuse with a high electrokinetic potential. By increasing  $\text{NaCl}$  concentrations, this part of charges decreased due to the effect of salt concentration in reducing the electrokinetic potential of the Diffused Double Layer (DDL). Regarding to the divalent cation  $\text{Ca}^{2+}$ , the results indicated that as the concentration of  $\text{CaCl}_2$  increase in the solution; the electrokinetic potential as well as the DPC of Ca-Bentonite decrease. In addition, by increasing  $\text{NaCl}$  equivalent fractions over  $\text{CaCl}_2$  the DPC increased. Finally, While  $\text{NaCl}$  was acting as an indifferent electrolyte;  $\text{CaCl}_2$  changed the electrokinetic properties of the interface.

**Keywords:** Electrokinetic potential, Ca-Bentonite suspensions, Electrolytes, Diffuse double layer charge.

The electrokinetic potential is one of the main parameters that determine clay particle stability in suspensions. An increase of the electrokinetic potential adds to the electrostatic repulsion between clay particles and thus stabilizes clay suspensions. The value of electrokinetic potential and thickness of the diffuse layer are controlled mainly by the following factors: clay surface potential; type of the exchangeable cations; concentration and chemical composition of the pore solution; dielectric constant of the solution, pH and temperature (Alexei, 2000).

Surface potential relationship around a colloidal particle play an essential role in determining the electrical behaviors of the clay particles (Hiroyuki, 2002 and Lagaly & Ziesmer, 2003).

*Clay particle electrical double layer structure*

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The distribution of the dissociated cations near a clay particle surface is determined by the balance between electrostatic attraction of the clay surface and thermal motion of the ions tending to spread the ions away from the surface and equalize their concentration in the solution. The part of the clay surface (or thermodynamic) potential which is compensated by the adsorbed cation layer, is called consequently the adsorption potential. The remaining part of the potential, at the boundary between adsorbed and diffusion layers, is called Stern potential (Gregory, 1989).

In this paper, the electrokinetic potential, surface potential and the diffuse particle charge behaviors in the double layer of Ca-Bentonite towards some electrolytes will be examined and the effect of absolute and fraction concentrations of  $\text{CaCl}_2/\text{NaCl}$  on the above properties will be studied.

### Material and Methods

This work included two experiments; the first experiment was carried out using 5% clay suspensions into different NaCl or  $\text{CaCl}_2$  equivalent concentrations. The range of these concentrations was between 0-100 meq/L. The second experiment was achieved using different equivalent fractions of  $\text{NaCl}/\text{CaCl}_2$  in a separate series to study the interactions between these two ions onto the diffuse part of the double layer. The two experiments were carried out under constant conditions of moisture, temperature, particle size, pH and surface potential.

#### *Apparatus*

The Mütek PCD-03 Herrsching/Germany Particle Charge Detector combined with an automatic titration installation (DL 25 METTLER TOLEDO GieBen/Germany) was used in measuring the electrokinetic potential and surface charges. It is a streaming current detector, which has the capability of charge measurements at high conductivity.

#### *Procedure*

There are no direct methods for determining thermodynamic or stern potentials. Instead of the Stern potential, the electrokinetic or zeta potential ( $\zeta$ ) is often used for calculations. Consequently, the electrokinetic potential of clays can be found by means of electrophoresis or electro-osmosis techniques.

The aqueous suspended sample was placed in the measuring cell. Once the PCD was turned on, the piston of the cell oscillated and caused a high flow rate. Any charged material adsorbed to the cell wall was separated from its counterions by the flow and created a streaming current. Two golden electrodes in the cell picked up this current and displayed it on the unit. A polyelectrolyte (polydiallyl-dimethylammonium chloride, Ploy-DADMAC, molecular weight about  $10^4$ - $10^5$  g) of an opposite charge was titrated until reaching the zero point of charge. The electrokinetic potential was measured immediately before titration.

This potential represents the potential of the plane of shear between the Stern and Gouy layers, *i.e.*, Stern Potential. This technique has been used in many works (Miller, 1996 and Bocbenhoff *et al.*, 1997). Then, the measurement procedure facilitate the determination of the charges into the EDL of the clay. The measured potential at the starting point represents the electrokinetic potential. By starting titration with the cationic polymer (poly-DADMAC) the charges into the double layer will be neutralized. This amount of charge represents the diffused and non-diffused EDL charges. Where the electrokinetic potential or zeta potential is the plane of shear between the diffused and the non-diffused layers. So, it is possible to separate the two part of charges throughout this technique, which depends mainly on the following equations (Sparks, 2002).

$$\sigma = - \int_0^{\infty} \rho \, dx \quad (1)$$

Where:  $\sigma$ , total charge and  $\rho$ , space charge density ( $C/m^3$ ) is given by:

$$\begin{aligned} \rho &= \sum C_i Z_i F \\ &= C_+ Z_+ F - C_- Z_- F \end{aligned} \quad (2)$$

Where:  $C_+$  and  $C_-$  are the local molar concentration of the cations and anions,  $Z_+$  and  $Z_-$  are the valence of cations and anions respectively and  $F$  is Faraday constant.

The total charge in equation (1) is due to charges in two layers

$$\sigma = (\sigma_1 + \sigma_2) \quad (3)$$

Where:  $\sigma_1$  is the Stern layer charge and  $\sigma_2$  is the diffused layer charge.

The relationship between the permanent charge ( $\sigma_p$ ) electrolyte concentration ( $C_o$ ) and surface potential ( $\phi_o$ ) can be identified from equation (4):

$$\sigma_p = \left( \frac{2 C_o \epsilon RT}{\pi} \right)^{1/2} \sinh \frac{zF \phi_o}{2RT} \quad (4)$$

In this system surface charge density is controlled by lattice defects in the interior of the crystal, so that double-layer potential,  $\phi_o$ , electrolyte concentration,  $C_o$ , dielectric constant,  $\epsilon$ , temperature,  $T$  and counter-ion valence,  $z$ , are not able to influence the sign or magnitude of the surface charge. Therefore equation (4) becomes

$$\left( \frac{2 C \epsilon RT}{\pi} \right)^{1/2} \sinh \frac{zF \phi_o}{2RT} = \text{constant} \quad (5)$$

so that change in electrolyte concentration, dielectric constant, counter-ion valence, or temperature is counteracted by reduction or increase of surface potential. The reduction in potential is accomplished by the compression of the double-layer. The degree of the double-layer compression is governed by the concentration and valence of the counter-ions, whereas the effect of co-ions is comparatively small (Sparks, 2002).

## Results and Discussion

### *The origin of surface charge*

Here we first summarize the different types of process that lead to charge separation at interfaces and the resulting formation of double layers. Electrokinetic properties are greatly affected by edge faces. Active hydroxyl sites are located on these planes. The surface of a colloid particle in an electrolyte solution is almost always electrically charged. There are three main mechanisms responsible for the charging of the surface: (i) ion adsorption, due to which ionic charge is taken from the electrolyte solution to the surface; (ii) surface dissociation, *i.e.*, departure of ions from the surface and their transfer to bulk electrolyte solution; and (iii) isomorphous replacement of ions of the solid phase by others of a different charge, which is accompanied by sorption of electrons from outside, (Fig.1).

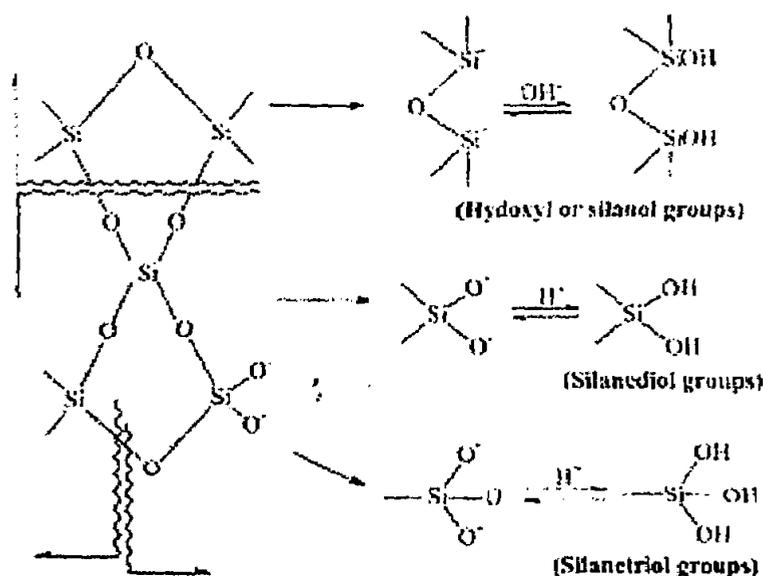


Fig. 1. Broken bonds and surface charge development in clay minerals.

The electrokinetic potential measurements revealed that Ca-Bentonite surface acquires negative charges. This negative charge results from substitutions within the Bentonite lattice, the broken bonds at the Si-O-Si (siloxane group) of Bentonite particularly generated at the particle surface during grinding, (Fig. 1) and the lattice imperfections (Breck, 1974; Grim, 1968 and Van & Roolefson, 1991). Also Bentonite can be considered as a permanently charged mineral because of the isomorphous substitution.

In aqueous environments, hydration reduces the strength of bonds between a clay surface and exchangeable cations (cations-compensators or counterions). While some of the cations remain attached to the clay surface and form the adsorbed cation (or so-called Stern) layer, others transit at some distance from the clay surface and form the diffuse ionic layer.

The electrical field of a charged surface attracts the ions of opposite sign (counterions) and repels the ions of the same sign of the particle (co-ions), originating the screening of the particles' charge by the free ions in the solution. As a result, the whole system, *i.e.*, the charged particle, together with its screening charge, reach a state of electroneutrality, which is characterized by the space separation of the particle's surface charge and the ionic charge screening it. The electroneutral system consists of spatially separated charges. The charge localized on the surface of the colloid particle and the screening charge localized in the adjacent electrolyte solution form the electric double layer of the colloid particle (Alkan *et al.*, 2005; Bahri & Mehmet, 2002 and Caballero & Shilov, 2002).

#### *Calculation of surface potential*

According to equation (4) surface potential ( $\phi_0$ ) was calculated at different NaCl and CaCl<sub>2</sub> concentrations and different values of permanent charges measured by PCD. The calculated values of  $\phi_0$  are presented in Table 1.

**TABLE 1. Surface potential at different electrolyte concentrations.**

Electrolyte type and concentration (meq/L)	Permanent charge $\sigma_p$ (C/m <sup>2</sup> ) x 10 <sup>-3</sup>	surface potential $\phi_0$ (mv)
NaCl		
20	74	107
40	67	95.5
60	55	72
80	42	54.6
100	15	20
CaCl <sub>2</sub>		
20	37	40.6
40	31	29
60	28	23.5
80	26	19
100	22	15

The results in Table 1 indicated that increase electrolyte concentration, counter-ion valence, or temperature is counteracted by reduction of surface potential. The reduction in potential is accomplished by the compression of the double-layer. The degree of the double-layer compression is governed by the concentration and valence of the counter-ions, whereas the effect of co-ions is comparatively small (Sparks, 2002).

#### *Effect of NaCl concentrations on the diffuse charges of Ca-Bentonite*

The data of PCD showed that at low NaCl concentration 0.01 M/L the charges increased as Na ions made the double layer more diffused comparing with Ca ions. By increasing NaCl concentration, this part of charges decreased due to the effect of salt concentration in reducing the electrokinetic potential of the Double Layer (Fig. 2, 3& 4).

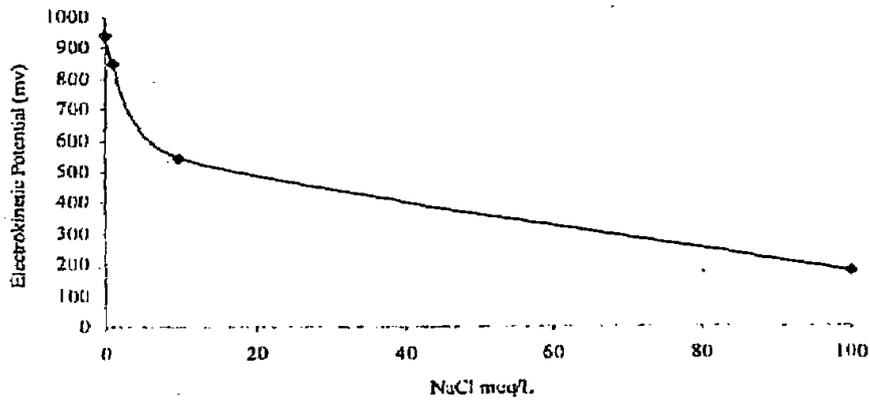


Fig. 2. Effect of NaCl concentration on the electrokinetic potential of Ca-Bentonite.

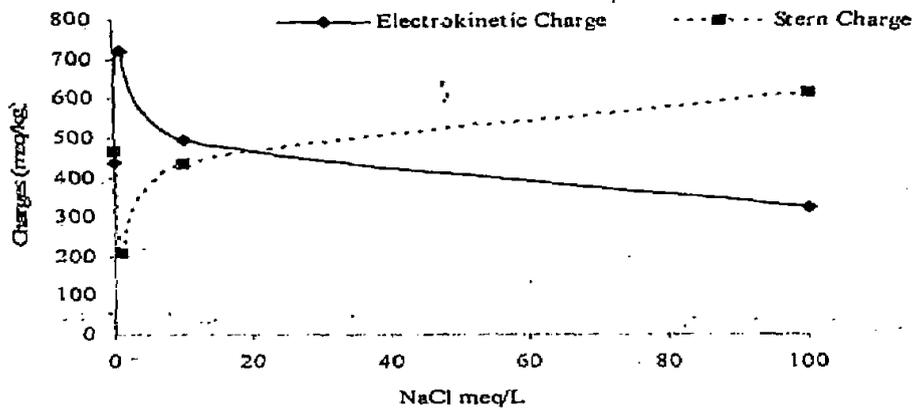


Fig. 3. Effect of NaCl concentration on the electrokinetic and Stern charges of the diffused part of the double layer of Ca-Bentonite.

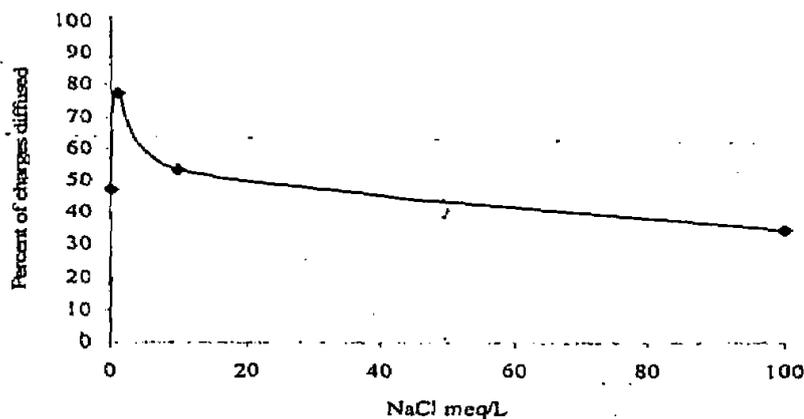


Fig. 4. Effect of NaCl concentration on the percent of charges diffused of Ca-Bentonite.

Due to compression of the double-layers at increasing electrolyte concentrations, the range of repulsive force is considerably reduced (Fig. 3). The repulsive energy or the repulsive potential is the amount of work required to bring the particles from infinite separation to a given distance between them. Repulsive force can also be manipulated by changing the valence of the counter-ion. The attractive energy is independent of concentration and valence of the counter-ion. Maximum flocculation is induced at high concentration, when repulsive energy decays rapidly and attractive force becomes dominant. Thus, the colloidal stability is determined by the balance between the repulsive and attractive forces which the particles experience as they approach each other. Zeta potential ( $\zeta$ ) or electrokinetic potential is the electric potential developed at solid-liquid interface in response to movement of colloidal particles in one direction (toward positive pole) and counter-ions into another direction (low and negative pole). The thickness of the double-layer affects the magnitude of the electrokinetic potential. Thus, the electrokinetic potential decreases with increasing electrolyte concentration (Fig.2), (Sparks, 2002).

The effect of monovalent electrolytes such as NaCl on the diffuse charges of Ca-Bentonite showed a reduction in the electrokinetic potential as electrolyte concentration increased. This result is in a good agreement with other literatures (Dogan *et al.*, 1997; Kelly & Spottiswood, 1982; Bahri & Mehmet, 2002 and Alkan *et al.*, 2005). The reduction in the electrokinetic potential of Ca-Bentonite in the presence of Na<sup>+</sup> ion can be explained in the following manner: the monovalent counter ions are known as indifferent electrolytes (Hunter, 1993) excluding the ion exchange mechanism, they cannot adsorb specifically onto Ca-Bentonite and are not capable of causing a charge reversal. Because of the coulombic attraction they only accumulate as counter ions in the electrical double layer (EDL). Consequently, they compress the EDL and change the magnitude of the electrokinetic potential of Ca-Bentonite.

As seen in Fig. 2,3 and 4, the surface is, at first, more negatively charged, and then the negative charge decreases as the concentration of electrolyte increases. It can be said that the effect of monovalent cation, *i.e.*, Na<sup>+</sup> on the electrokinetic potential and charges of Ca-Bentonite in a wide range concentrations is not pronounced. This may be due to the exchange of monovalent cation (Na<sup>+</sup>) with divalent cations (Ca<sup>+2</sup>) present in Ca-Bentonite. The ion-exchange process is a stoichiometric reaction and thus is generated by the equivalent amounts of cations to maintain the total electroneutrality at the solid-solution interface. Consequently, the exchange of Na<sup>+</sup> with divalent cations like Ca<sup>+2</sup> and in Ca-Bentonite requires two Na<sup>+</sup> ions for electroneutrality. Therefore, the ion-exchange capacity of Ca-Bentonite for monovalent cations appears only at high concentrations of NaCl (Bahri & Mehmet, 2002 and Alkan *et al.*, 2005).

*Effect of CaCl<sub>2</sub> concentrations on the diffuse charges of Ca-Bentonite*

Figures 5,6 and 7 show the change of the electrokinetic potential and charges of Ca-Bentonite with electrolyte concentration in the presence of divalent electrolytes, CaCl<sub>2</sub>. The results revealed that as the concentration of CaCl<sub>2</sub> increase in the solution; the electrokinetic potential as well as the diffused charges of Ca-Bentonite decrease. Note that at high CaCl<sub>2</sub> concentrations, Ca-Bentonite tends to give charge reversing. Indeed, charge reversal requires, in addition to ion exchange, specific adsorption of counterions in EDL, namely, in the inner Helmholtz plane (IHP) of the Stern layer. As divalent cations such as Ca<sup>+2</sup> reverse the sign of the surface, this cation specifically adsorbed onto Bentonite. This ion can be adsorbed in the Stern layer, namely the outer Helmholtz plane (OHP), or in the diffuse layer. It is also assumed that this cation may specifically adsorb in the IHP of the stern. However, it can reduce the surface potential by charge neutralization and in turn compress the thickness of the EDL with a reduction in the electrokinetic potential (Bahri & Mehmet, 2002 and Alkan *et al.*, 2005).

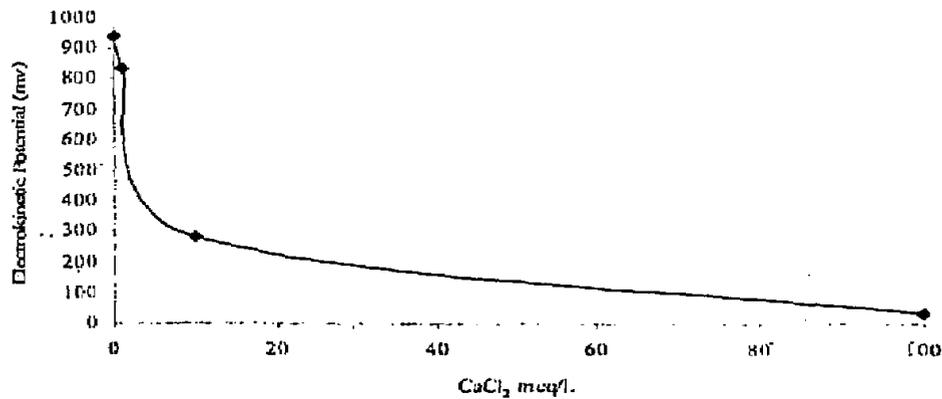


Fig. 5. Effect of CaCl<sub>2</sub> concentration on the electrokinetic potential of Ca-Bentonite.

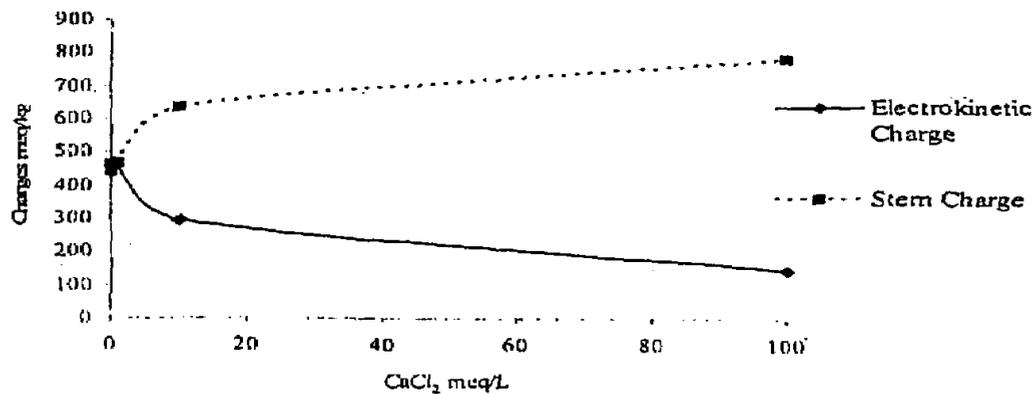
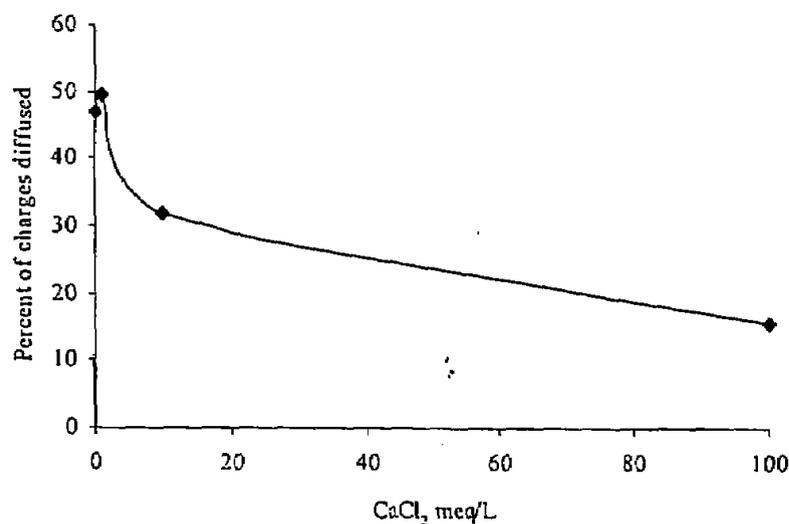


Fig. 6. Effect of CaCl<sub>2</sub> concentration on the electrokinetic and Stern charges of the diffuse part of the double layer.



**Fig. 7.** Effect of  $\text{CaCl}_2$  concentration on the percent charges diffused.

*Influence of  $\text{CaCl}_2$  and  $\text{NaCl}$  equivalent fractions on the Diffuse Particle Charges of Ca-Bentonite*

The results indicated that, by increasing  $\text{NaCl}$  equivalent fractions over  $\text{CaCl}_2$  the diffused particle charges (DPC) increased. This behavior is due to the properties of hydration and polarizability of these ions on the Double Layer of Bentonite.

The variation of electrokinetic potential and charges as a function of the equivalent fraction for  $\text{NaCl}$  and  $\text{CaCl}_2$  solutions is shown in Fig. 8,9 and 10. While  $\text{NaCl}$  acts as an indifferent electrolyte (does not change the surface potential of clay particles themselves but affect the thickness of the EDL)  $\text{CaCl}_2$  changes the electrokinetic properties of the interface. Generally, if the other physico-chemical conditions (moisture, temperature, particle size, pH, surface potential) are constant, the increase of salt concentration causes reduction of the double ionic layer and decreases the electrokinetic potential (Gregory, 1989). This is explained by the fact that, if the salt concentration in the pore solution increases, some of the cations move from the diffuse layer to the adsorption layer and consequently the electrokinetic potential decreases, Fig. 2 and 5. Since specific adsorption of divalent cations almost always involves proton exchange, an important characteristic of this adsorption process is the number of protons released, or hydroxide ions adsorbed, for each cation adsorbed means that the surface charge becomes increasingly positive, which is reflected in a change in the electrokinetic properties of the interface Fig. 8,9 and 10. In this case, the specific adsorption reverses the sign of the effective charge of the surface.

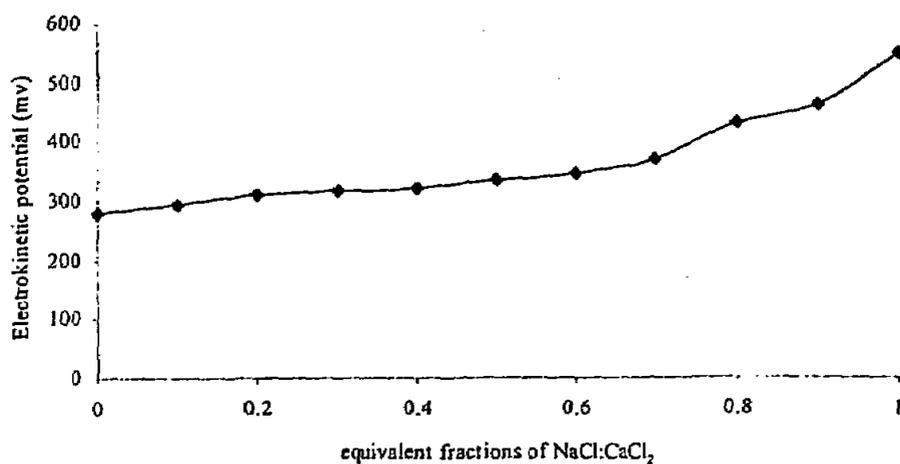


Fig. 8. Effect of NaCl:CaCl<sub>2</sub> equivalent fractions on the electrokinetic potential of Ca-Bentonite.

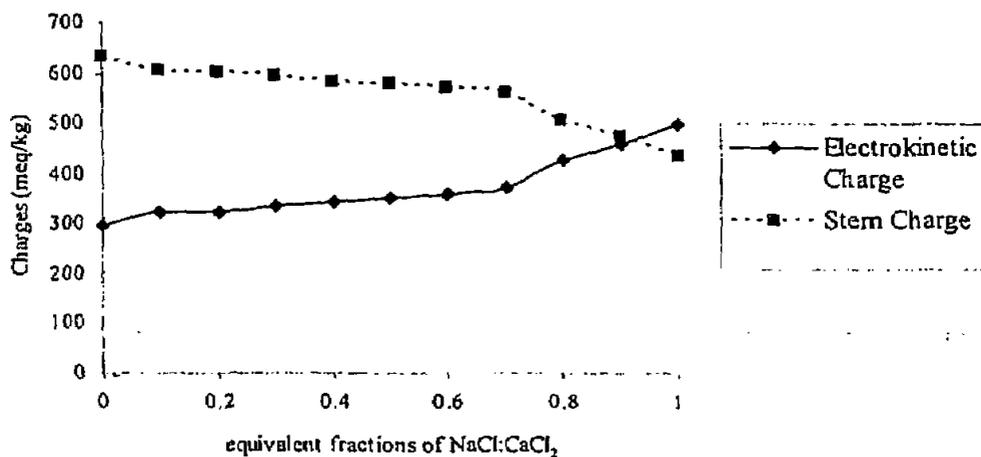


Fig.9. Distribution of double layer at NaCl:CaCl<sub>2</sub> equivalent fractions.

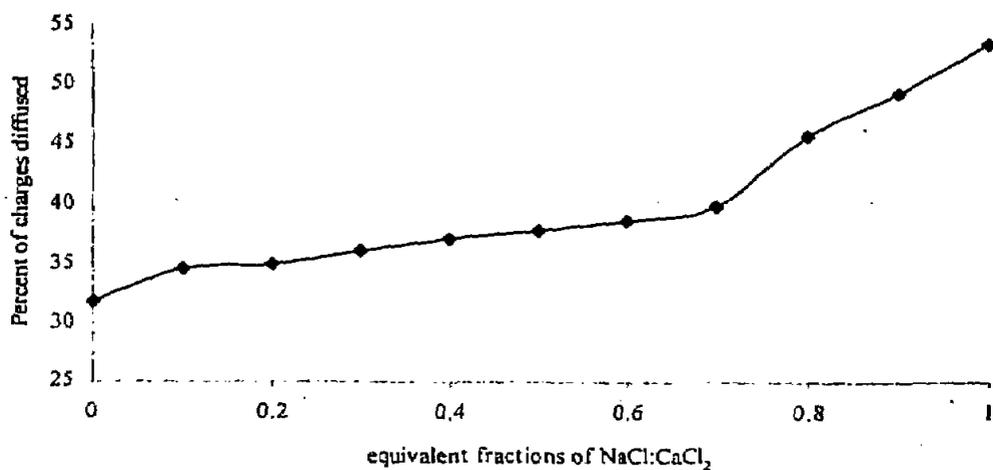


Fig. 10. Effect of NaCl:CaCl<sub>2</sub> equivalent fractions on the percent of charges diffused (electrokinetic charges).

### Conclusion

Monovalent electrolyte can only compress the EDL and reduce the electrokinetic potential. In addition to be incorporated and specifically adsorbed in the EDL the divalent cations are able to reverse the surface charge due to the high ability of ion exchange and relatively low levels of specific adsorption. It may be said that many of the experimentally observed clay colloid properties may be at least qualitatively described in terms of simple electric double-layer model. The clay colloid properties which can be successfully described by the double-layer theory include surface charge, cation exchange capacity, buffering capacity, and colloidal stability. The important solution properties will include, the electrolyte type (valence), composition and concentration.

The versatility of electric double-layer theory is further evident from its ability to qualitatively explain charge behavior in permanent charge systems.

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## كثافة الشحنة السطحية و علاقتها بجهد الحركة الكهربائية لمعدن البنتونيت الكالسيومى فى وجود إلكتروليات أحادية و ثنائية التكافؤ

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فى هذا البحث تم دراسة توزيع جهد الحركة الكهربائية (الجهد الزيتي) وشحنة الحبيبات المنتشرة (DPC) فى الطبقة الكهربائية المزدوجة لمعدن البنتونيت الكالسيومى نحو بعض الإلكترونيات أحادية أو ثنائية التكافؤ مثل كلوريد الصوديوم و/ أو كلوريد الكالسيوم. أيضاً تم دراسة تأثيرات تلك الإلكترونيات سواء كانت فى تركيزات مطلقة منفردة أو تركيزات متكافئة الأجزاء على معدن البنتونيت الكالسيومى. أظهرت النتائج زيادة فى الشحنات عند تركيزات منخفضة (0.01 مول/لتر) من إلكتروليات كلوريد الصوديوم أحادى التكافؤ حيث أن أيونات الصوديوم توسع من الطبقة الكهربائية المزدوجة و تجعلها أكثر إنتشاراً بجهد زيتي مرتفع.

أما زيادة تركيزات كلوريد الصوديوم أدت إلى إنخفاض كثافة هذا الجزء من الشحنات و ذلك نتيجة تأثير تركيز الملح فى خفض الجهد الزيتي للطبقة الكهربائية المزدوجة. ومن جهة أخرى أوضحت النتائج أنه بزيادة تركيز إلكتروليات كلوريد الكالسيوم ثنائى التكافؤ حدث إنخفاض فى كل من الجهد الزيتي و DPC لمعدن البنتونيت الكالسيومى. بالإضافة إلى ذلك وجد أنه بزيادة التركيزات متكافئة الأجزاء لكلوريد الصوديوم عن كلوريد الكالسيوم حدث إنخفاض فى DPC. وبحساب الجهد السطحي بدلالة الشحنات الدائمة أظهرت النتائج أن الجهد السطحي ينخفض كلما زاد تركيز الإلكترونيات أحادي أو ثنائي التكافؤ. الخلاصة هى أن إلكتروليات كلوريد الصوديوم يؤثر على سمك الطبقة الكهربائية المزدوجة أما كلوريد الكالسيوم يؤثر على خواص الحركة الكهربائية للسطوح البينية للحبيبات.