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Electrophoresis of Suspended Kaolinite in Multivalent Electrolyte Solution

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Zeta potential is known as the electrical potential at the shear plane and is one of the important electro-osmotic properties of clay minerals. For many applications, the sign and the magnitude of the zeta potential is necessary to be known. For clay soils, it is usually negative. In present study, zeta potential of kaolinite clay immersed in various electrolytes namely; $CaCl_2$, $Al_2(SO_4)_3$, H_3PO_4, Na_2Sio_3, and Na_2Co_3 at different electrolyte concentration is investigated. As a result, the pH strongly altered the zeta potential of kaolinite. Also, zeta potential and specific conductivity have ranged from -86 to +204mV and 1450 to 15900µs/cm, respectively, at pH 2 to 9.3. In addition, pure kaolinite yields in an isoelectric point (IEP) at pH ~ 3.15.Although, there was no IEP for particles suspended in $CaCl^2$ solution, a shift in IEP towards alkaline part observed when kaolinite particles immersed in $Al_2(SO_4)_3$ as well as H_3PO_4 solution.

Keywords: Zeta potential, surface charge, isoelectric point, kaolinite, multivalent electrolyte.

1. INTRODUCTION

Interaction of mineral particles with inorganic and organic compounds is deeply depending on their chemical, surface charge properties, mineralogical and on environmental characteristics such as concentration of electrolytes, pH and temperature [1-4]. As for clay mineral particles, surface charge is including negative structural charge, which is rather is not affected by both the ionic strength and pH as well as variable (pH and ionic strength dependent) charge of the edges [5-6].

In addition, the study of physico-chemical properties of liquid/colloid particles interfaces is important for optimization of a large number of geo-environmental engineering applications including contaminant removal, stabilization, and ion migration [1, 3], decontamination [7-8] and electroosmotic dewatering [4, 9].

Electrokinetic properties of charged particles in colloidal systems such as the IEP has a remarkable influence in realizing the adsorption steps of inorganic and organic compounds at the interface of solid particles immersed in solution and liquid [10-11]. For example, flotation and coagulation mechanisms as well as dispersion mechanism resulted from such adsorption processes. Accordingly, selection of appropriate flotation species required to understand effect of different type of collector adsorption on soil particles, their minerals and their activation mechanisms [12]. As for coagulation, an important issue in most of suspensions separation processes such as waste water treatment systems, is to find zeta potential behaviors of solid/liquid solution and their IEP as well [14-16].

Chemical species led to interaction in EDL of kaolinite particles. It is due to high pH dependency of negatively surface charge of kaolinite colloidal particles [17-19]. Such interaction will effect the current flocculation and coagulation mechanism of kaolinite solution. The more flocculation processes occurring through the soil, the higher permeability will be made and also higher electroosmosis phenomena dominate rather than ion migration of amendment.

Although the characteristics of zeta potential of cement system have been studied extensively [4, 5, 9, 17-19], few studies conducted in the relationship between the interaction of EDL in the various multivalent cations in kaolinite.

The main objective of this research is to investigate the difference of zeta potential between the single system of kaolinite colloid and the binary systems containing various multivalent ions.

2. MATERIAL AND METHODS

2.1. Zeta Potential Measurements

Zeta potential is able to present valuable data regarding surface and particle charges in surfactant solutions according to different electrolytes and electrolyte concentrations as well.

To determine the zeta potential of the kasolinite suspensions, Zeta Meter 3.0 model were used to conduct electrophoretic mobility measurements (Fig. 1).Smoluchowski's equation is utilized in the Zeta meter instrument to determine electrophoretic mobility of the colloidal particles suspended solution and convert it to the zeta potential value.

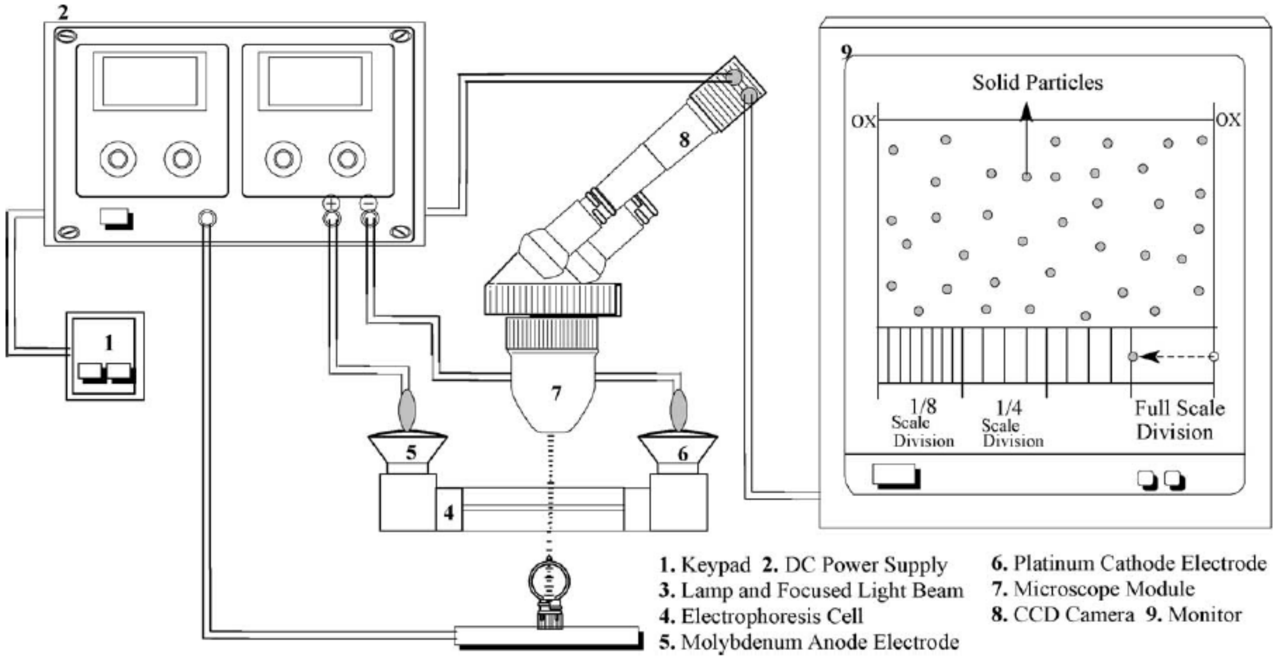
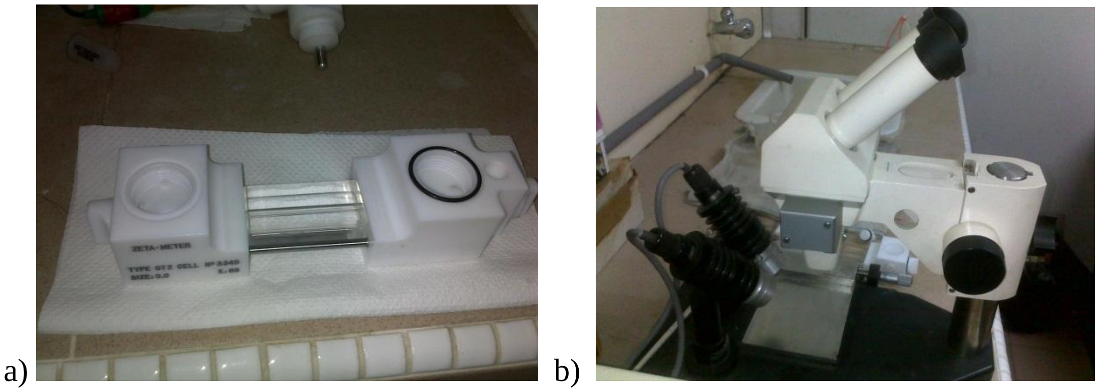


Figure 1. General schematic of Zeta Meter 3.0. (Zeta Meter Inc., Staunton, VA, USA)

This equation is the most famous expression for zeta potential measurement, which provides a direct relation between electrophoretic mobility and zeta potential [16]. The zeta potential was calculated according to Eq. (1).

$$\zeta = \frac{u\eta_t}{\varepsilon_0 \varepsilon E} \qquad (1)$$

Where, u is the particle velocity, η the viscosity, ε the relative permittivity of the pore fluid, and ε_0 the permittivity of free space and E, the field strength. The schematic view of the zeta meter equipment is presented in the Figure 2.



a) b)

Figure 2. Zetameter Equipment (a) Electrophoresis cell, and (b) Zeta meter

2.2. Sample preparation

Kaolinite was collected as hand specimen from a deposit near Selangor-Malaysia. Zeta potential measurements were conducted based on immersing 100 mg/L concentration of solids in liquid. By using a magnet stirrer; the solution was stirred until the solution find constant pH. As for pH of the solution, before and after each measurement the pH was measured and if any changes happened in pH, the last one was considered. Standard deviation used for zeta potential measurement to determine reliability of the recorded zeta potential. Moreover, for each measurement the standard deviation was less than 2mV, which is automatically calculated by the zeta meter instrument. The zeta potential of at least ten particles for each sample was determined and their average was taken. The room temperature was 24±2.5 ◦C.

3. RESULTS AND DISCUSSION

Zeta potential versus pH relationship for pure kaolinite is presented in Figure 3. The zeta potential of pour kaolinite soils varied from +9.87 mV at pH ~ 2 to -13.5 mV at pH ~ 12. It should be mentioned that the zeta potential was zero at pH ~ 3.05 (Fig. 3). The variations in zeta potential with pH were probably related to the nature of electrical energy field in kaolinite soils [20-24]. This might be considered as generation of variable charge mechanism since the surface positive charge of kaolinite increased with decreasing the suspension pH, however, due to the protonation of surface hydroxyl groups on kaolinite, their surface negative charge tend to decrease [4, 15, 23]. It is well understood the change in zeta potential in colloid suspensions come from change in surface charge and under acid conditions, kaolinite carried net negative surface charge. The zeta potential showed the negative value for the kaolinite system when pH higher than 3.1 (Fig. 3).

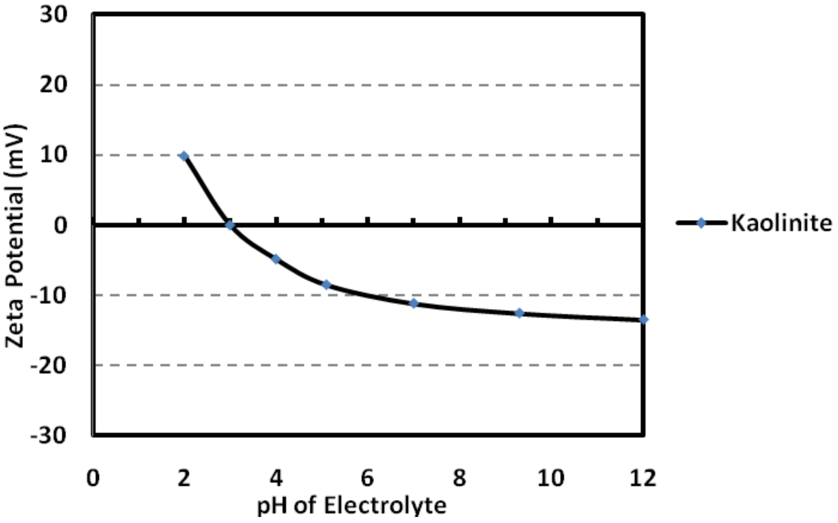


Figure 3. Zeta potential - pH relationship for suspended kaolinite in distilled water

Effect of varoius electrolyts and their concentrations on the zeta potential of kaolinite suspension are provided in Figure 4 to Figure 8. The pH of solution showed remarkably effect over the uptake of stabilizer reagent. It determines speciation of the adsorbed species, types of potential determining ions, degree of ionization and surface charge of the solid particles [18, 25-28].

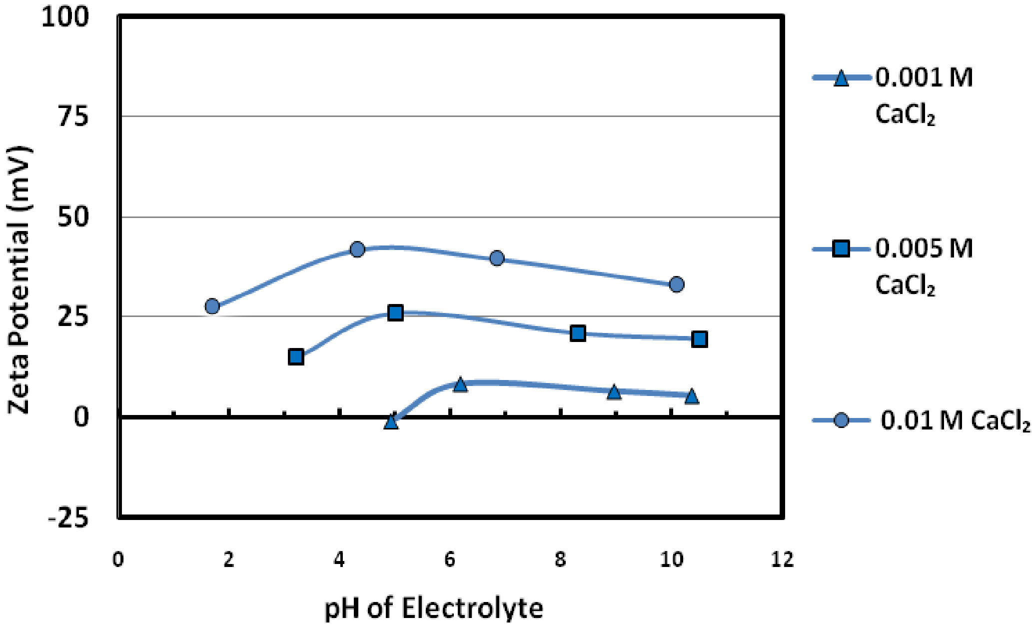


Figure 4. zeta potential of kaolinite suspended in $CaCl_2$ solution

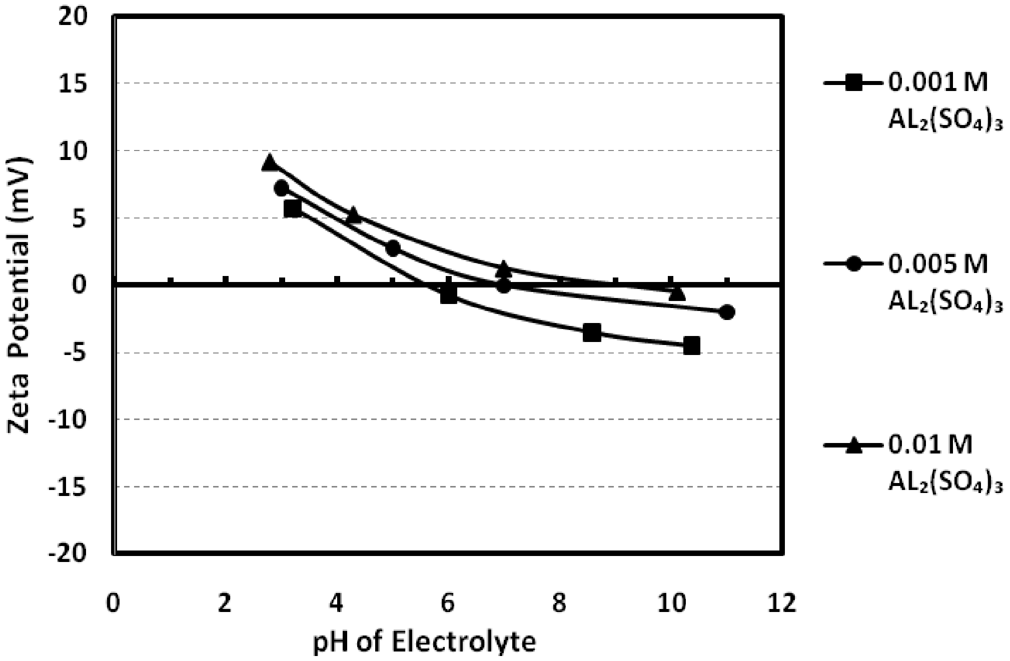


Figure 5. zeta potential of kaolinite suspended in $Al_2(SO_4)_3$ solution

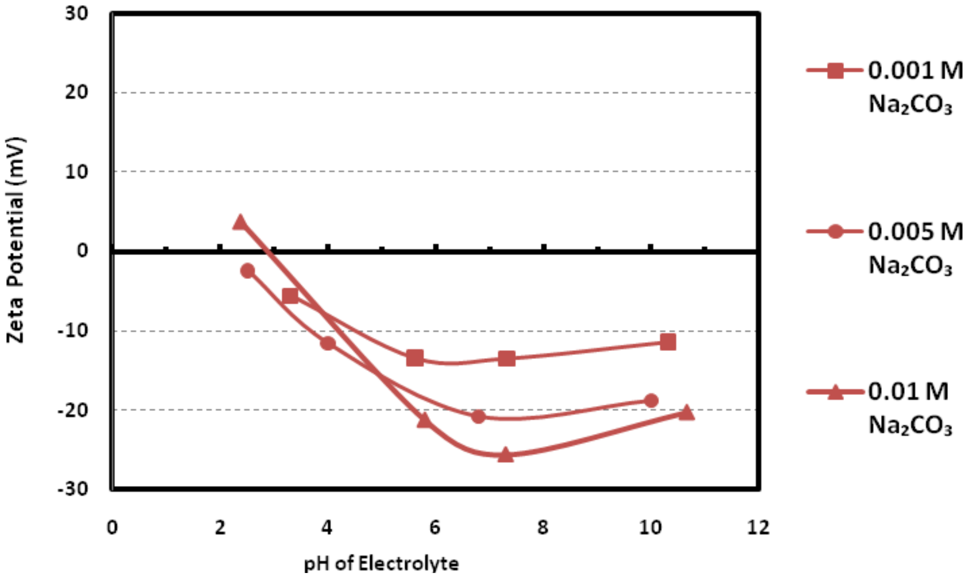


Figure 6. Zeta potential of kaolinite suspended in Na_2CO_3 solution

As showed, not only kaolinite suspention pH is significantly depend upon electrolyte type and its concentration, dissociation also is in a direct relation with chemicals additives. This means the charge is affected by solution pH as well.

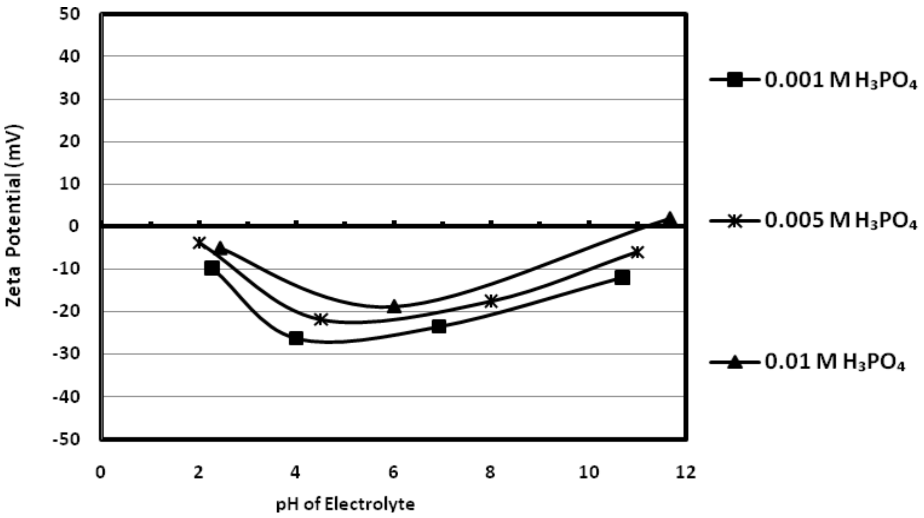


Figure 7. zeta potential of kaolinite suspended in H_3PO_4 solution

For kaolinite immersed in $Al_2(SO_4)_3$ (Fig. 5), Na_2CO_3 (Fig. 6), and Na_2Sio_3 (Fig. 8), as the pH went up, the net negative charge was produced and as the pH decreased, there was less and less negative charge, however, zeta potential showed reverse trend with pH when kaolinite immersed in

$CaCl_2$ (Fig. 4) as well as H_3PO_4 (Fig. 7). It is noteworthy that the, zeta potential behavior of $CaCl_2$ solution showed a peak value of 8.32, 26.08 and 41.83 mV at electrolyte concentration of 0.001, 0.005 and 0.01 respectively. The more electrolyte concentration led to less pH regarding their peak values as for $CaCl_2$ pHs related to the peak were 6.18, 5 and 4.3 at 0.001, 0.005 and 0.01 electrolyte concentration, respectively (Fig. 4). The zeta potential value of $CaCl_2$ is significantly affected by the electrolyte concentration. This can be due to changing in the dehydrated calcium ions concentration in the inner Helmholtz plane, ascribed variations in the dissolution rate.

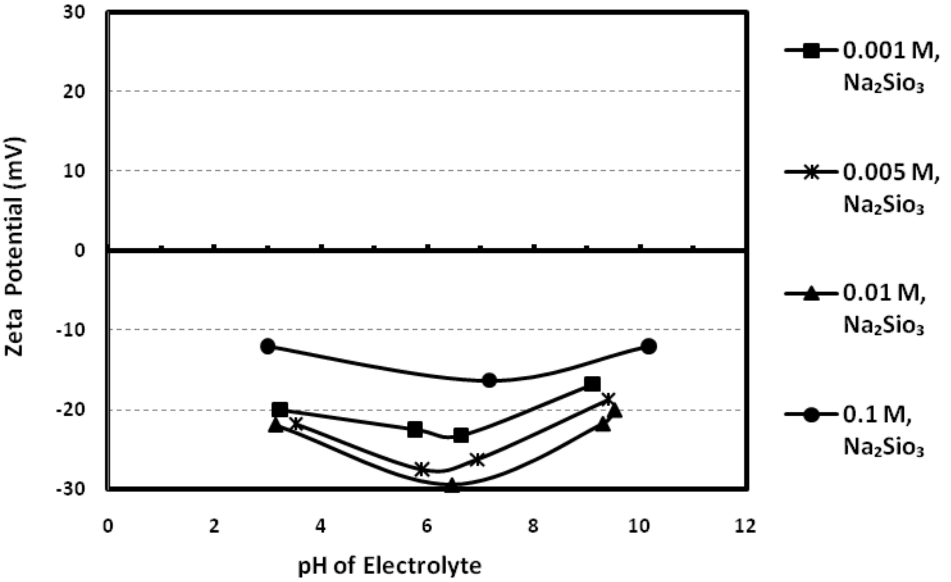


Figure 8. zeta potential of kaolinite suspended in Na_2Sio_3 solution

The zeta potential of kaolinite particles suspended in $Al_2(SO_4)_3$ solution at electrolyte concentrations of 0.001, 0.005, and 0.01 M were 5.1, 6.91, and 8.32 respectively (Fig. 1), in their natural pHs which were 3.2, 3.13, and 3.05 respectively. Considering the zeta potential sign, observed results clearly show that electrolyte concentration has significant change in the increasing positive zeta potential values in acidic part and negative values in alkaline part (Fig. 4 to Fig. 8). On the other hand, values of zeta potential in all solution samples increased typically with the increase in pH, except for Na_2Sio_3 solution and pure kaolinite that reverse behavior have observed. Regardless the sign of zeta potential, the natural zeta potential of the immersed kaolinite soils increased with higher electrolyte concentration such as 0.01 and 0.1 M except for Na_2Sio_3 which were almost constant during electrolyte increment. It could be due to negative charge in available silicate in such chemical reagent. Moreover, effect of electrolyte concentration on solution pH was not as remarkable as zeta potential values since in all chemical species solution pH did not change significantly during concentration increment but their zeta potential considerably different and increased remarkably. This was more evident in order of

$CaCl_2 > Al_2(SO_4)_3 > Na_2CO_3 > H_3PO_3$ and Na_2Sio_3. It should be mentioned that the thickness of double layer in 0.1 mol/L concentration of $CaCl_2$ was more than that can be calculated according present von Smoluchowski theory [4, 16]. Theories on electro-osmotic flow suggest that decreasing the diffuse double layer decreases electroosmosis [4, 29-33]. Results clearly proved that in the kaolinite soils, higher electrolyte contents had more influence over increase of the natural zeta potential in comparison with reagents having less electrolyte content. Thus, the relationship between electrolyte concentration and zeta potential are not only under influence of electrolyte concentration contents, but also under influence of electrolyte and pH.

The increase in the zeta potential values after 0.01 M electrolyte concentration may be due to the expansion of the electrical double layer. Cations like Ca^{2+}, Al^{3+} and Na increase the electrical double layer thickness and thus increase the value of natural zeta potential.

3.4. Effect of electrolytes on isoelectric point of kaolinite

The electroosmotic flow can virtually be eliminated at the IEP point. Therefore, elimination of electroosmotic flow in the kaolinite soils suspended in water can be expected at pH 3 to 3.3 however adding different chemicalss caused a shift in pH at IEP towards to the acidic part at pH~1.8 to 2.1 or alkaline part at pH ~ 8.5 to 9 (Fig. 9).

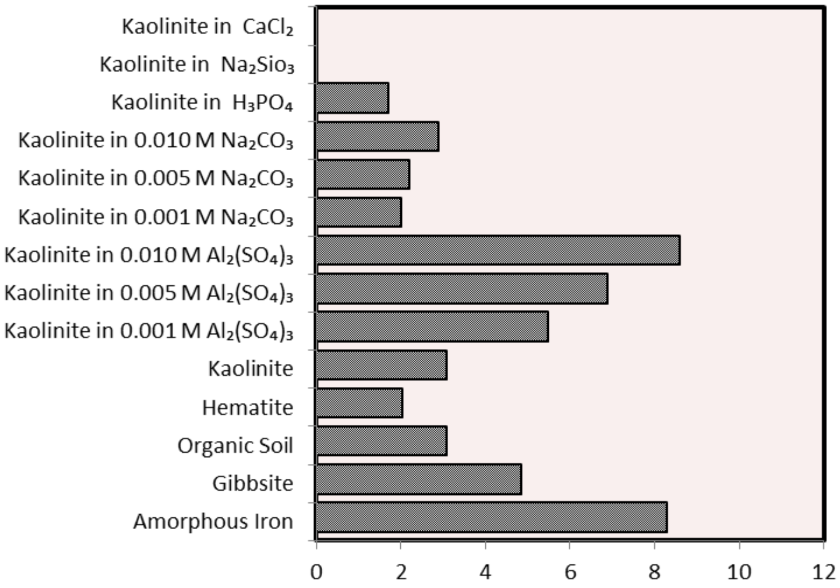


Figure 9. pH at IEP of variable charge soil by comparison with the some minerals

On the other hand, negative surface charge of particles (negative zeta potential) causes electroosmotic to occur from anode to cathode, while positive surface charge causes electroosmotic to occur from cathode to anode [14, 34-36]. When the net charge is zero, soil particles in soil water suspension will not repel each other but will tend to aggregate and form larger particles [7, 10, 37-38]. This effect in turn will contribute to an increase in soil permeability through the soils. In contrast, negatively charged soil particles repel each other, resulting in dispersion and decrease in soil permeability [9, 12, 18, 38]. Figure 9 shows the values of IEP of some minerals in comparison with kaolinite soils immersed in multivalent cations that used thorough this study. Since all charge in humus is strongly pH-dependent, the sensitivity of the highly organic soils such as peat to pH changes in EK phenomena is more than mineral soils like kaolinite [29-30]. Despite this high sensitivity, the IEP point of kaolinite soils immersed in H_3PO_4, and Na_2Co_3 as depicted in Figure 9 was less than amorphous iron, gibbsite, as well as organic soil and pure kaolinite. Thus, the consistency of flow direction in tropical soil immersed in such electrolytes may be more probable than that in mineral soils (Fig. 6). It should be mentioned that IEP could not be observed for $CaCl_2$ and Na_2Sio_3 electrolytes due to their positive and negatively electrical charge consistency, respectively.

A difference in the IEP between different samples having the same chemical formula has been often attributed to the differences in their crystallographic structure and degree of hydration [31]. In general, multivalent ions, polymers, and surfactants tend to adsorb specifically and shift the IEP. The magnitude of the shift depends on the solid to liquid ratio.

The shift in the IEP is commonly negligible when the amount of the solute in the system is small compared with the proton charge [3, 16]. This explains the discussed above difference in the IEP obtained by means of electrophoresis on the one hand and electroacoustics on the other, namely, in electrophoresis (small solid to liquid ratio) traces of the impurities in solution, e.g. silicates leached out of the glassware, may induce a substantial surface coverage and thus a shift in the IEP [24, 31, 38-39]. In other words, the pristine IEP obtained in the absence of specific adsorption are also valid for sufficiently low concentration (compared with the proton charge) of specifically adsorbing ions.

When the concentration of the solute is high enough, its specific adsorption may (but not necessarily does) induce a shift in the IEP. In addition, specific adsorption of anions induces a shift in the IEP to low pH for materials having a high pristine IEP (e.g. aluminum oxides, iron and hydroxides) [1, 5, 8]. Specific adsorption of cations changes the EK curves of materials having a low pristine IEP [30].

5. CONCLUSIONS

Electroosmotic behavior of kaolinite is important to study since it has a wide variety of application in engineering projects especially for selecting a suitable grout as stabilizer. Zeta potential is one of the very important physicochemical properties of minerals which interact with grout reagents. In present research the zeta potential and IEP of kaolinite in various solutions were determined. Based on the results of this study, the following conclusions may be drawn:

- The kaolinite surface in water has a net negative charge at the natural pH of the suspension whereas, zeta potential varied from +9.87 mV at pH ~ 2 to -13.5 mV at pH ~ 12. The zeta potential was zero at pH ~ 3.05.
- As for $CaCl^2$, zeta potential of the suspensions substantially increased in pH ranged from 2.0 to 6.0 in positive sign which means thickening the DDL. In such a case injecting mostly will be carried out based on electroosmotic flow and that is far from ion migration. The higher electrophoretic mobility led to more grouting movement through soil and this should be considered as a key factor for cases that whether settlement under available building is allowable or not.
- Zeta potential has showed a range between -4.5 to +41.83mV at pH 2 to 10.4 changing with $Al_2(SO_4)_3$, and $CaCl_2$. Although, there was no IEP for $CaCl^2$, H_3PO_4, and Na_2sio_3 solution, a shift in IEP towards alkaline part found when kaolinite immersed in $Al_2(SO_4)_3$.

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