Int. J. Electrochem. Sci., 6 **(2011)** 4493 - 4503

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Zeta potential of Organic soil in Presence of Calcium Chloride, Cement and Polyvinyl Alcohol

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Received: 16 March 2011 / *Accepted:* 2 September 2011 / *Published:* 1 October 2011

In this study the influence of varoius dosage of cement, polyvinyl alcohol (PVA), and calcium chloride ($CaCl_2$) on the zeta potential of organic soil has been examined. Two different PVA species were used, fully hydrolyzed (PVA-F) as well as partially hydrolyzed (PVA-T). As results, adding the PVA and cement dosage into the suspended colloids led to an increase of zeta potential in their surfaces, contrary to measuring done in water. In absence of $CaCl_2$, zeta potential of organic soil immersed in PVA or cement showed a range between +22 to +211 mV at pH ~ 1.7 to 11.3, while, in presence of $CaCl_2$ the variation of zeta potential was in a range of +25 to -110mV at pH ~2.2 to 10.3. Although, there was no IEP in presence of $CaCl_2$ additives, a peak in zeta potential was observed for organic soil immersed in various electrolytes. Moreover, iso-electric point (IEP), for soil samples suspended in water is at pH about 3.1 to 3.3. However, the IEP of organic soil when is suspended in cement and/or PVA solution significantly decrease to the values about pH~1.9 to 2.0.

Keywords: Cement, polyvinyl alcohol, zeta potential, isoelectric point, organic soil.

1. INTRODUCTION

Many of the key properties of colloidal systems are determined directly or indirectly by the electrical potential on the particles. The charge distribution itself determines the interaction energy between the colloidal particles, and this is many cases responsible for the particles' stability towards coagulation and for many aspects of the flow behavior of the colloidal particles suspension [1-4].The Stability of such particles is determined by the charge that they exert on their diffuse layers as well as the distance of the ions in the electrical double layer which come from the surface of the colloid. Unstable colloid also can get much closer together than stable colloids [5-6]. The stability of the colloidal particles is affected by several factors; the surface area, the size, and the surface charge. Surface charge in turn is a function of dissolved salts concentration and pH [7]. On the other hand, long-range particulate structures of dispersed and agglomerated systems are closely associated with interparticle forces between the different mineral particles. Measurements of the zeta potential are commonly used to determine the interparticle forces [3, 8].

In recent years, the demands placed on ordinary Portland cement concretes have greatly increased. The zeta potential of pure cement particles is small. However, both positive and negative values can be found in the literature [9-12]. The addition of super plasticizers typically induces negative zeta potentials. For strong electrolytes, values are between -20 mV and -30mV. For weaker electrolytes, as PEO containing copolymers, values can be as small as -5 mV [10, 12].

Furthermore, polymers generally are macromolecular compounds with more than 1,000 atoms. They consist of a large number of small, self-repeating molecular units (monomers). The monomers can be used in different aggregate forms, as liquids, solids, or gases, to produce a virtually infinite number of possible variants of polymers [13]. Water based polymers such as polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), and carboxymethyl cellulose (CMC) are known to be eco-friendly polymers and are widely used as stabilizers in pharmaceuticals, cosmetics etc [13-15]. Polyvinyl alcohol or PVA fibers are high performance synthetic fibers used mostly for reinforcing concrete mixes. PVA is an organic material made from carbon, hydrogen, and oxygen. PVA is a white soluble high molecular compound produced from vinyl acetate by polymerization. Some of the desirable physical properties of PVA fibers are excellent tensile stress, high modulus of elasticity, mouldability, and impact strength [14-16]. PVA fibers will also develop a strong bond on the molecular level with the cementitious mixture during the concrete curing [17].

Although the characteristics of zeta potential of cement system have been studied extensively [9-10, 12, 18-21], few studies conducted in the relationship between the interaction of EDL in the mixture of cement and PVA with $CaCl_2$ in organic soil. The main objectives of this research is to investigate the difference of zeta potential between the single system of organic soil colloid and the binary systems containing cement and/or PVA, in presence of $CaCl_2$ as a salt ions.

2. MATERIAL AND METHODS

Soil samples were collected in accordance with the British Standard Institution [22] methods of test for soils (BS 1377-1:1990) from Mardi, Selangor, Malaysia. The pH, water content, specific surface area, and zeta potential were measured in accordance with BS 1377-3:1990, BS 1377-2 1990, BET technique, ASTM D 4187, respectively. The CEC of soils also was measured at pH 7 with ammonium acetate [23].

2.1. Soil Sample Purification

The solid sample was dried for 24 h at 105°C, ground, and then sieved by a 75-μm sieve. For the electrophoretic mobility measurements, the suspensions were prepared in a polyethylene container by mixing 0.1 g of the soil sample with 100 ml of double-distilled water with a specific conductivity of 1.4µS/cm, after adding the desired concentration of cement and PVA. organic soil samples were treated before their use in the experiments. In order to obtain homogenized organic soil colloidal particles: The suspension containing particles (100 mg L^{-1}) were mechanically stirred for 24 h. After agitation for 30 min in a shaker, the suspension was allowed to stand for 25 min to let the larger particles settle.

2.2. Zeta Potential Measurements

To determine the zeta potential of organic soil, electrophoretic mobility measurements were conducted using a Zeta Meter Model 3.0^+ (Zeta Meter Inc., USA). The instrument, using Smoluchowski's equation, determines the electrophoretic mobility of the particles automatically and converts it to the zeta potential [24]. The zeta potential measurements were measured as a function of pH, and adsorbed amount of cement or PVA on the surface of colloidal particles. After adsorption period, we measured the zeta potential of particles which were obtained by centrifuging the suspension. For the zeta potential measurements, a 50mg sample was transferred into aqueous solution and the soil particles mixed homogenously with a magnetic stirrer. All the measurements were carried out therefore at 100 mg/L solid concentration. The voltage to be applied is determined based on the specific conductivity of the solution. The particle movement is observed through a microscope and the time taken for a particle to travel a particular micrometer distance is measured. To minimize reading error, a minimum of 10 particles are tracked and their average time is calculated. The pH was adjusted in the range from 2to 11 before each measurement by drop wise addition of 10^{-3} N and 10^{-1} N of NaOH as well as HCL. The pH that was observed after the zeta potential measurement was recorded as the final pH. The pH measurements were carried out using a Mettler–Toledo Model MP220 pH meter combined with a Mettler–Toledo Model InLab 413 pH electrode. Boiled and double-distilled water was used to prepare aqueous solutions for all experiments to measuring zeta potential.

3. RESULTS AND DISCUSSION

3.1. Test material properties

Type II Portland cement (ASTM C1501) from Lehigh Portland Cement Co. (Allentown, PA) was used in present research. The chemical oxide compositions as determined by using X-ray fluorescence and chemical analysis was found to be: C_aO, 63.83%; SiO_2, 21.63%; Al_2O_3, 2.02%; Fe_2O_3, 4.48%; MgO, 1.92%; SO_3, 1.61% and the loss of ignition was 2.2%. Its specific gravity was 3.15 x 10^3 kg/m^3 and BET, specific surface 0.786 m^2/g. Physico-chemical properties of organic soil soil samples also showed in Table 1.

Table 1. Physico-chemical properties of organic soil samples

Parameter	organic soil	Standard
Color	Brownish	
Moisture content,%	158	BS 1377-2 1990
Soil pH	6.65	BS 1377-3:1990
Specific surface area, m^2/g	46	BET technique
CEC, meq/100 g soil	85	After Chapman, 1965
Organic content %	58	BS 1377-3: 1990
Zeta potential, mV	-64.3	ASTM D 4187

3.2. Zeta potential Vs. pH of pure organic soil

The zeta potential of organic soil suspended in water varied from +25.1mV to -95.4 mV at pH 2.8 and 11.3, respectively. Also, zeta potential for organic soil was almost zero at pH 3.25 to 3.35 (Fig. 1).

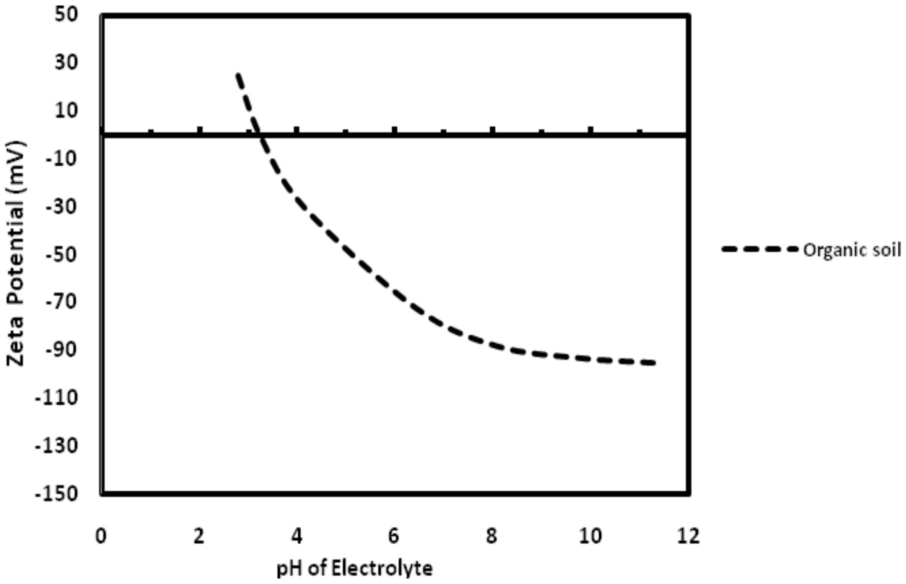


Figure 1. Zeta potential - pH relationship for organic soil

For organic soil, as the pH went up, the net negative charge was produced and as the pH dropped, there was less and less negative charge (Fig. 1). Moreover, the variations in zeta potential with pH could be related to the nature of electrical energy field in organic soil. The natural pH of organic soil was equal to 5.63 where zeta potential showed -63.6mV. Highly negative charge of organic soil is due to strong pH-dependent behavioral of humic substance which behaves like polyprotonated weak acid [7, 25]. However, organic soil suspention pH is significantly depend upon concentration of electrolyte type, and dissociation are also in a direct relation with chemical reagents. It means the charge is affected by pH [25-27].

3.3. Effect of polyvinyl alcohol and cement on surface charge of organic soil

Zeta potential of suspended organic soil in cement, PVA-F, and PVA-P showed in Figure 2. For this stage, $CaCl_2$ was not included to the solution. The zeta potentials for organic soil -cement was varied from +24.2mV to -88.12mV at pH of 1.7to 10.3, respectively. However, a peak observed in pH~6.1 with zeta potential equal to -110.2mV.Also, zeta potential for organic soil was almost zero at pH ~ 1.9 to 2.0 (Fig. 2).The zeta potentials for organic soil -PVA showed a more variation with pH according to the percent of PVA hydration. The zeta potentials for organic soil immersed in PVA-F was varied from +10.7mV to -60.19mV at pH of 1.9 to 11.53, respectively.

The variation for organic soil immersed in PVA-P was much higher and it was varied from +39.5mV to -110.22mV at pH of 1.85 to 10.35, respectively (Fig. 2).

This can be attributed to the increasing molecular attraction between the organic soil particles and PVA-F with increasing degree of saponification due to the formation of hydrogen bonds. PVA-P shows inferior compressive and flexural strength to PVA-F due to the presence of ester group which interrupts the formation of hydrogen bond. Also, this could probably due to specific behavior of organic soil (as a variable charge soil) to adsorb ions. Variable charge soils generally carry both positive and negative charges, and soil can adsorb cations as well as anions [7, 17, 25, 27-29]. The adsorption can be electrostatic and/or specific in nature.

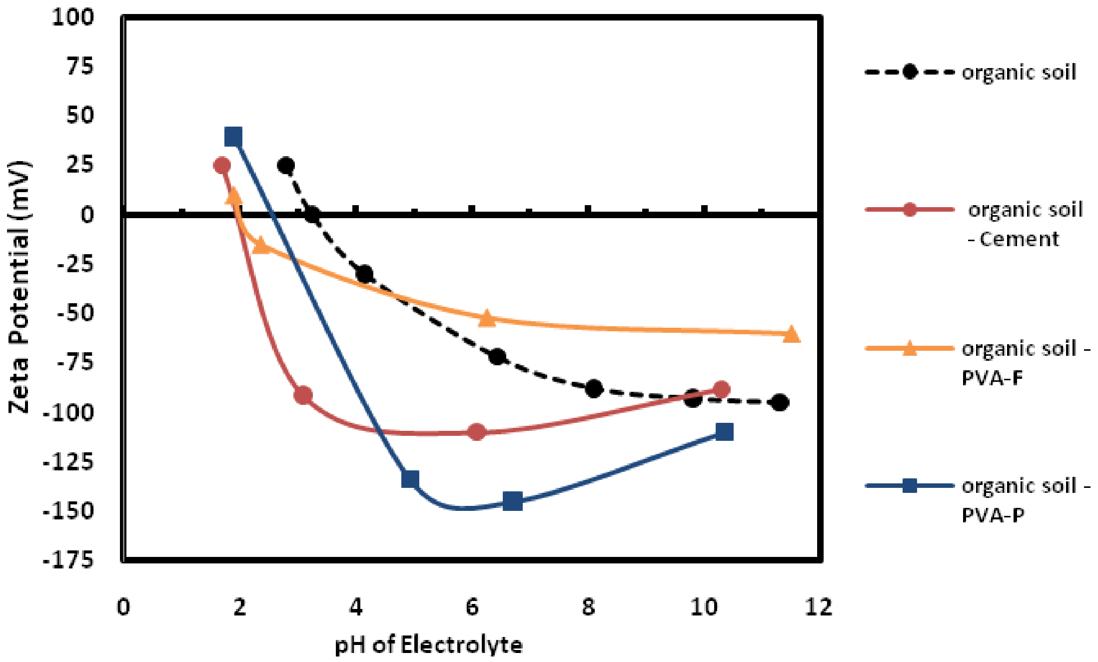


Figure 2. Zeta potential of suspended organic soil in Cement, PVA-F, and PVA-P

One important consequence of specific adsorption of anions is that the adsorption may result in a decrease in positive surface charge and/or an increase in negative surface charge of the soil [7, 27, 30-32].

This kind of effect has been found to induce changes in electrokinetic properties of these soils when they specifically adsorb inorganic anions [33-35]. Effect of cement as well as PVA on zeta potential of organic soil in their natural pHs presented in Figure 3. In contrast with the cement and PVA-F, the PVA-P had more tents to increase the zeta potential. The zeta potential for organic soil immersed in cement, PVA-F, and PVA-P was -88.12, -51.98, and -134.1mV in their natural pH at 10.3, 6.26, and 4.94, respectively (Fig. 3).

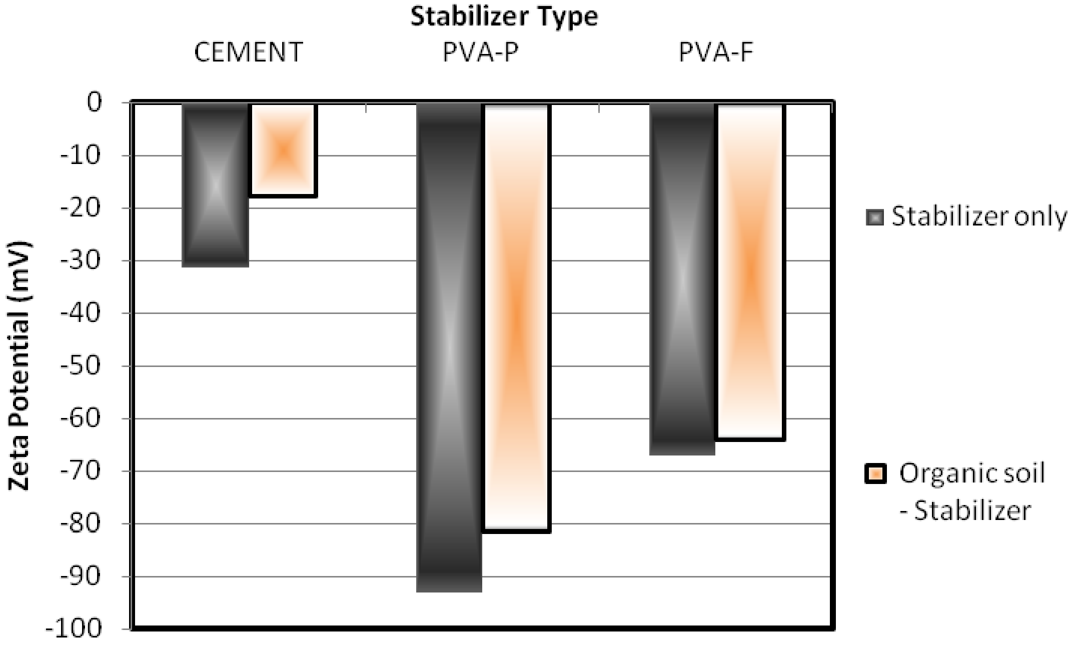
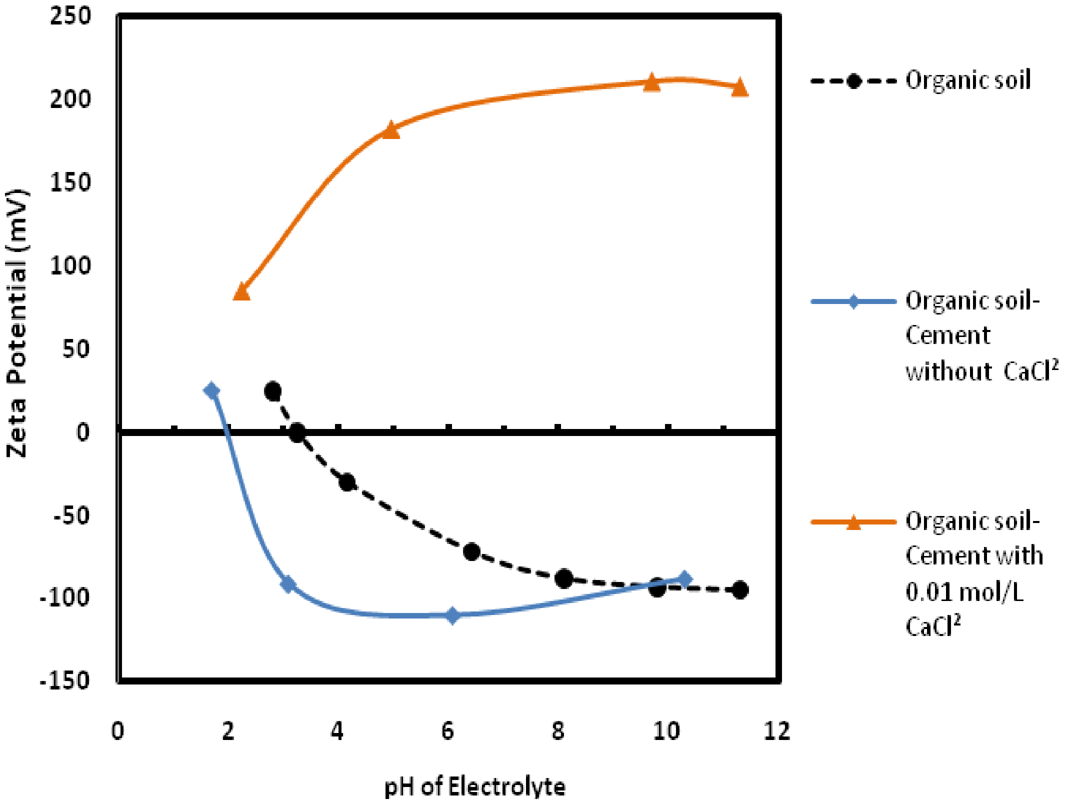


Figure 3. Effect of cement and PVA on zeta potential of tropical organic soil in its natural pH

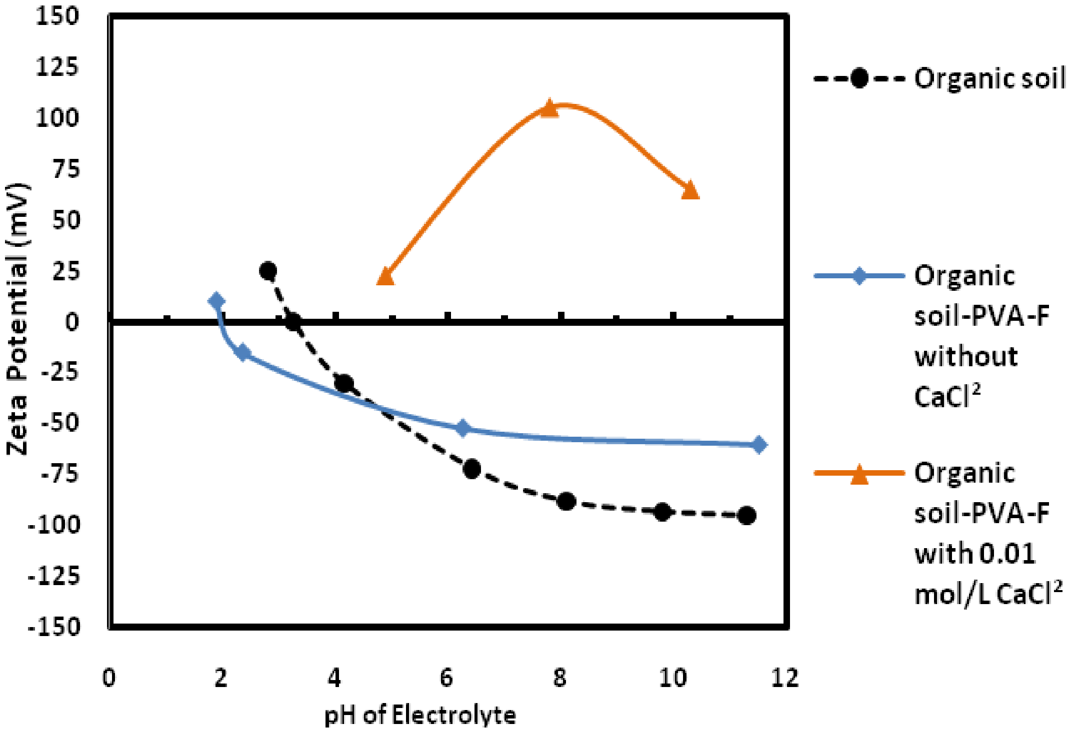
3.4. Effect of calcium chloride on the zeta potential of organic soil immersed in cement and PVA

Figure 4 show the zeta potential of organic soil particles as a function of pH for various concentrations of cement (Fig. 4.a), PVA-F (Fig. 4.b) and PVA-P (Fig. 4.c) with and without 0.01 mol/L $CaCl_2$ dosage.

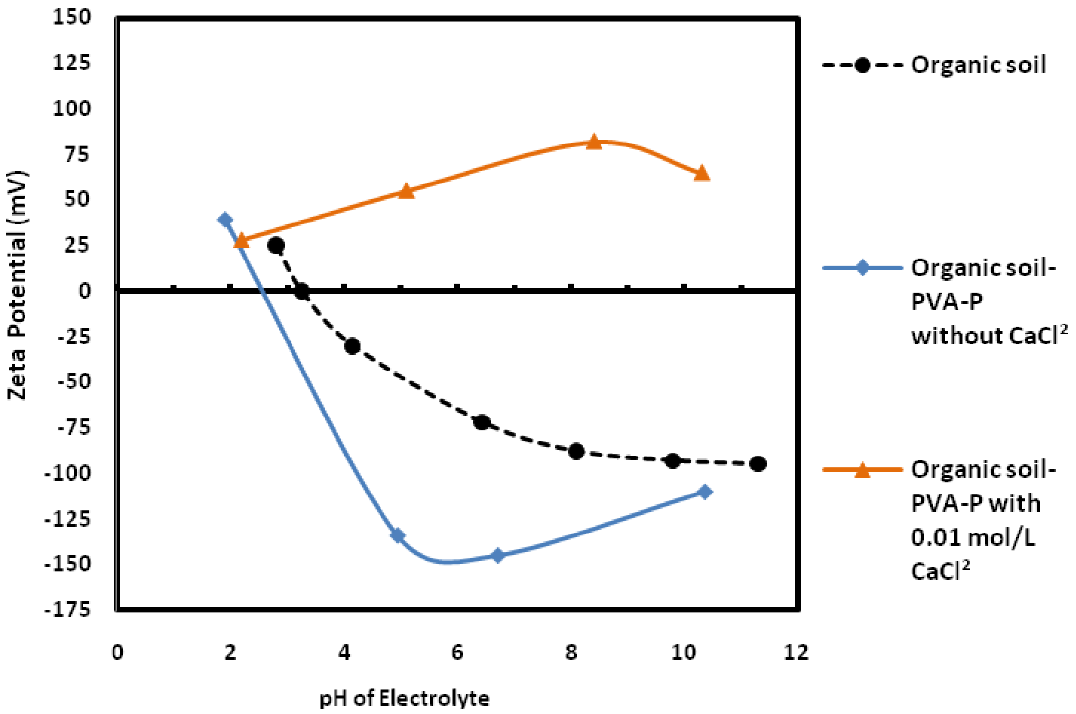
Observed results clearly show that $CaCl_2$ has significant influence in the increasing zeta potential of organic soil immersed in cement as well as PVA. The zeta potential showed quite sensitive to small additions of electrolyte both at high and low pH. In this range the adjustment of pH is sufficient to significantly influence the ionic strength. On the other hand, zeta potential behavior of $CaCl^2$ solution showed a peak value of +211, +105 and +82 mV for cement, PVA-F, and PVA-P stabilizer in their pH at 9.7, 7.8, and 8.4, respectively. This could be due to changing in the dehydrated calcium ions concentration in the inner Helmholtz plane, ascribed variations in the dissolution rate [7]. However, the relationship between electrolyte concentration and zeta potential are not only under influence of electrolyte concentration contents, but also under influence of electrolyte and soil types.


250
200
150
100
50
0
-50
-100
-150
Zeta Potential (mV)
0
2
4
6
8
10
12
pH of Electrolyte
Organic soil
Organic soil-Cement without CaCl²
Organic soil-Cement with 0.01 mol/L CaCl²

(a)


150
125
100
75
50
25
0
-25
-50
-75
-100
-125
-150
Zeta Potential (mV)
0
2
4
6
8
10
12
pH of Electrolyte
Organic soil
Organic soil-PVA-F without CaCl²
Organic soil-PVA-F with 0.01 mol/L CaCl²

(b)



(c)

Figure 4. Effect of CaCl² dose on zeta potential of organic soil immersed in (a) cement, (b) PVA-Fsolution, and (c) PVA-Psolution

3.5. Effect of polyvinyl alcohol and cement on isoelectric point of tropical organic soil

No IEP was observed as for kaolinite particles immersed in $CaCl_2$ solution (Fig. 4 and Fig. 5). This is in agreement with the previous studies which no IEP was obtained with neither for monovalent cations nor divalent cations [5, 18, 26, 36-38]. This is probably due to difference in dissolution of OH^- ions compared to the H^+ ions in organic soil solution when it is immersed in $CaCl_2$ solution.

Figure 5 shows the values of IEP of some minerals in comparison with organic soil from this study [27]. A difference in the IEP between various samples having the same chemical formula has been often attributed to the differences in their crystallographic structure and degree of hydration [36-40]. In general, multivalent ions 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 always negligible when the amount of the solute in the system is small compared with the proton charge [36, 40]. 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 [5].

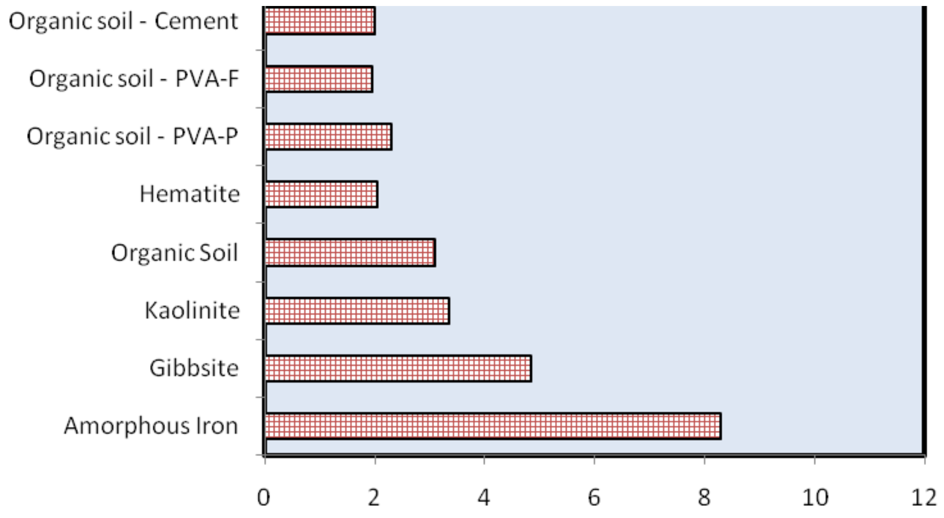


Figure 5. pH at IEP of variable charge soil by comparison with the some minerals

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 [39, 41-42]. Also, specific adsorption of anions induces a shift in the IEP to low pH for materials having a high pristine IEP (e.g. iron and aluminum oxides and hydroxides) [32, 35, 43-46].

4. CONCLUSIONS

In present research we explore zeta potential of organic soil immersed in cement as well as PVA in presence of $CaCl_2$. Based on the results of this study, the following conclusions may be drawn:

- Zeta potential organic soil immersed in PVA or cement showed a range between +22 to +211 mV at pH 1.7 to 11.3 in presence of with $CaCl_2$. However, the variation of zeta potential was in a range of +25 to -110mV without $CaCl_2$. Also, there was no IEP for $CaCl_2$ solution,
- Without $CaCl_2$ dosage and among the two types of PVA used in this research, fully hydrolyzed PVA (PVA-F) showed the lower zeta potential than partially hydrolyzed PVA (PVA-P). Also, similar trend observed for cement. However, in presence of $CaCl_2$, PVA-P showed lower surface charge potential than PVA-F. This is due to effect of Ca^{2+} ions from $CaCl_2$ which can significantly affect surface charge of organic soil from negative in alkaline part to the positive in both acidic and alkaline position.
- Organic soil particles surface immersed in water has a net negative surface charge at their natural pH and the IEP of them is at about pH 3.1 to 3.3. However, the IEP of them when they suspend through cement and/or PVA solution considerably decrease to the values about1.9 to 2.0.

ACKNOWLEDGMENTS:
Financial assistance from the Research Management Center (RMC) of the University Putra Malaysia (grant No. 91152) for conducting this experiment is gratefully acknowledged.

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