Characteristic Zeta Potential of Selected Oligocene-Miocene Shales from the Setap Formation, Onshore Sarawak-Malaysia

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Abstract

The zeta potential properties of sixteen shale samples deduced from electrophoretic mobilities of particles under the influence of an electric field have been studied and characterized in relation to clay mineralogy. Variations in zeta potentials were ascribed to differences in mineralogy, specifically the layered silicates. Two main groups have been delineated on the basis of clay mineralogy. Group-1 is mainly composed of the clay mineral kaolinite. Zeta potential generated in this group ranged from +24 mV to -60 mV. Positive charges have been ascribed to the protonation reactions on aluminol and silanol amphoteric sites of the dominant kaolinite clay mineral, and then the dissolution of aluminum ion from the crystal lattices of muscovite; a mineral that is common to all the nine samples that make up the group. Negative charges were due to deprotonation reactions on similar amphoteric edges of the dominant clay mineral. The average positive and negative zeta potentials assigned to samples in Group-1 are ~14 mV and 40 mV respectively. Kaolinite and illite are the main clay constituents of the second group. The combined effect of de/protonation reactions involving amphoteric sites on both kaolinite and illite, and then the dissolution of Al^{3+} from the crystal lattices of illite and muscovite, account for all negative and positive surface potentials respectively. The average zeta potential reported in this group is higher than that recorded in the former one but the average negative charges in both groups were comparable. Average IEP assigned to the Setap Formation in Malaysia is 4.69.

Keywords: Amphoteric sites, Kaolinite, Potential difference, Illite.

INTRODUCTION

Zeta potential is the potential difference generated due to the differences in particle ion concentration at the boundary of hydrodynamic shear or slipping plane [1]. It holds information on the electric double layer (Fig. 1) of charged particles [2]. The sign of these measurable electric data is similar to that of excess charged particles moving with the adhered layer of counter ions and the magnitude is proportional to the particle charge [2].

The theory of zeta potential is detailed by Müller [3], as such only a brief background is given here. Generally, particulate shales possess surface charges generated through mechanisms such as differential ion adsorption from an electrolyte solution, differential ion dissolution from a crystal lattice, surface anisotropy, isomorphous substitution and ionization of surface functional groups [4], the so-called Nernst potential. The degree of surface potential generation is known to a greater degree to be dependent on solution conductivity, electrolyte concentration, and pH, but it seems that the effect of pH is mostly a subject of most scientific discussions [5]. The dependence of surface potential on solution pH is important for the present study because, shale from the Setap Formation is composed of admixtures of clay minerals that bear variable charges [6]. The net charge on the shale particles affects the distribution of surrounding ions which results in an increase in the concentration of counter ions. The region of the extent of influence of such charge distribution is termed electric double layer (EDL) [3]. The EDL consists of an inner stern layer and an outer diffuse layer.

Particles movement in solution due to an applied voltage cause the diffuse layer to shorn off, hence particles obtain charge due to the loss of the counter ions. The potential difference at the plane of shear, i.e. zeta potential is the subject of interest of this study.
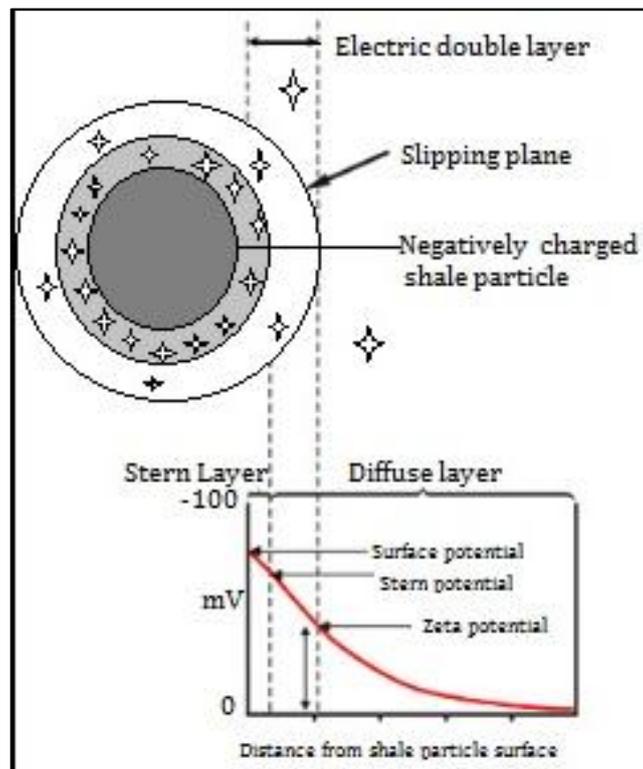
Figure 1: Schematic Representation of Zeta Potential. After Hunter [2]

The magnitude of the measured zeta potential is a good index of the magnitude of electrostatic repulsive interaction between shale particles and as such, can be used to predict and control the stability of the shale particles in a suspension [7]. Generally, the dividing line between a stable and an unstable suspension is within the range of $+30 \text{ mV} \geq \zeta \geq -30 \text{ mV}$. Every particle that fall outside this range is considered unstable. The point of least stability is when ζ is zero (0) and the pH of occurrence is termed *isoelectric point* (IEP)[8]. ζ is mostly deduced from electrophoretic mobility (EM) [4, 7]. Besides its experimental accessibility, the parameter is known to be intricately related to many geological processes in the petroleum cycle. Not only does the surface potential influence organic matter (OM) sequestration [9, 10], its interactions in aqueous solutions control ion exchanges, fluid flow rates [11], and are also known to be the single most contributing factor and primary dictator of pore fluid distribution and recovery rates of reservoirs [12].

The zeta potential of shale particles is seldom single and well-defined due to rock heterogeneities. Such heterogeneities in surface potential are mainly caused by complexities in the crystal structures and chemical composition of the shales. Foreign surface-bound materials like organic matter are additional sources of heterogeneities in surface potential. Due to the abundance of layered silicates and the existence of charges on their lamellae, clay minerals are known to account for most heterogeneities in variable surface potentials in shales [5, 13]. Measured surface potential due to clay minerals is mostly high in magnitude as compared to that from other

reservoir rocks, which might probably explain the occurrence of large quantities of hydrocarbon as 'sorbed gas' in shale gas systems [14, 15]. The types of clay minerals have also been shown to be a major player in influencing the sign and magnitude of surface potential that may be measured in shales. For instance, Tombácz and Szekeres [5, 16] showed that the 2:1 layered clays report relatively higher zeta potential than the 1:1 types do, although Taubaso et al. [17] have reported the reverse.

El-Swaify [18] and then Nmegbu and Spiff [19] have found the inextricable relationship between physicochemical properties of particulate matter in geological suspensions and zeta potential. For example, the sign and magnitude of zeta potential are known to govern important properties such as flocculation, coagulation, and aggregation [20]. This is an idea that has been exploited and successfully used to enhance oil recovery [19]. Zeta potential studies have also been used to estimate the amount of excess conductivity due to clay minerals in hydrocarbon estimation studies using resistivity logging [21, 22]. Despite their significance to the industry, data on ζ of hydrocarbon-bearing rocks is cripplingly non-existent. To aid in elucidating the theoretical aspect of problems involved and the practical application of zeta potential, this study intends to explore the characteristics, variations, and controls of the surface potentials of one of the primary hydrocarbon bearing Oligocene- Miocene shale units in Malaysia.

MATERIALS AND METHODS

Powders of sixteen (16) onshore samples (labeled S1-S16) from the Setap Formation have been analyzed for this study.

Mineralogical Analysis

Mineralogical compositions were derived from X-ray diffraction (XRD) patterns measured on randomly oriented powders. Analyses were performed on the fine fraction (<20 μm) from representative shale samples of uniform crystallite sizes achieved through milling with a Fristch-Pulveristte-2 mill and subsequent clay separation using procedures detailed by Macedo and Bryant [23].

Diffractograms were recorded in the 2θ in the range of 3˚-60˚with a scan speed of 1˚20/mm. All reported mineral compositions relate to the crystalline content of the analyzed samples.

Zeta Potential (ζ) Analysis

The ζ measurements were made with an Anton Paar Surpass™ Electrokinetic Analyzer (SEA) at 25 ± 0.1 ℃. The instrument is equipped with an attract software which automatically converts electrophoretic mobility of streaming potential of particles to ζ-potential using the Helmholtz-Smoluchowski equation- [1].

$$\zeta = \frac{4\pi V}{\varepsilon}\ EM \qquad [1]$$

Where, EM=electrophoresis mobility; V=viscosity of the suspension; ε =dielectric constant; Π= constant and ζ =zeta potential.

The procedure measures how fast charged particles move under the influence of an applied electric field. The bigger the charge particles carry, the faster the particles move. Stock dispersions were diluted to 0.05 g/l solid content and the salt concentration of dilute systems was adjusted to a constant concentration of KCl (0.001M). The pH of dilute dispersions was determined directly and adjusted with HCl and NaOH between 2 <pH> 10 before the introduction of samples into the capillary cell.

A titration unit in the Surpass™ measuring system which adjusts the pH of the sample suspension to pre-programmed values, and to selected rates of titration made IEP identification possible with commensurate precision with a single sample.

RESULTS AND DISCUSSION

Mineralogy and Surface Potential

A summary of sample pertinent physical properties is presented in Table 1. Clay mineralogical constituents of the samples are mainly kaolinite and illite. Distribution of these two clay minerals is mainly homogenous with kaolinite common to all the studied samples but, illite was reported in only seven of the samples. Based on these variations in clay mineralogy, the samples have been divided into to two main groups.

1)   Group-1

Group-1 is made up of nine samples (S1 to S9). The bulk mineral composition is fairly homogenous with quartz and kaolinite being common to all the samples. Slight variations within the group are the presence of pyrite in sample S9 and feldspar in samples S2 and S3 (Table 1). These are shown in the representative XRD diffractogram presented in Fig. 2 (*blue*).

The ζ fingerprints of samples from this group are presented in Fig. 3a to 3c. Apart from the sample S7 (Fig. 3b) that showed a slight increase in positive ζ at lower pH (<3), the absolute negative ζ of all samples in Group-1 decreased with decreasing suspension pH. The reverse is true for basic conditions. Reported ζ is within the range of -60 mV to +24 mV. The sample S1 (Fig. 3a) reported the highest positive (+24 mV) and negative (-60 mV) ζ. Variations in the generation of the amount of ζ are due to the differences in sample mineralogy and organic matter content.

The dependence of surface charge generation on pH has often been attributed to the protonation and deprotonation of potential determining ions on minerals surfaces [24]. In this study, however, surface negative charges (ζ) is interpreted as mainly due to dissociation reactions that occur at the surfaces of clay minerals. This is because, among the mineral constituents identified, the clay minerals are the most reactive. Surface reactions on kaolinite are likely to be dominant since the clay mineral is the most common and the major phase of the group (Table 1). As shown below in reactions [2] and [3], negative ζ on kaolinite-dominant shale particles arise from the significant contribution of amphoteric edge and basal (OH) (O face) sites through deprotonation from silanol and aluminol groups [4, 5, 25, 26].

$$\text{Si-OH} \longleftrightarrow \text{SiO}^- + \text{H}^+ \qquad (2)$$

$$\text{Al-OH} \longleftrightarrow \text{Al-O}^- + \text{H}^+ \qquad (3)$$

$$\text{Si-OH} \longleftrightarrow \text{SiOH}^{2+} \qquad (4)$$

$$\text{Al-OH} \longleftrightarrow \text{Al-OH}^{2+} \qquad (5)$$

At zero (0) ζ, the sign of all the samples but one (sample S9)(Fig. 3C) is reversed. This distinguishable pH values (IEP) at which ζ sign reversal occurred are presented in Table I. With the exception of sample S7 (Fig. 3b) that reported relatively high IEP, the range of IEP values are consistent with that reported for pure kaolinite using a similar methodology [27]. This confirms that the clay mineral is the determinant of surface charge characteristics within the group. The relatively high IEP reported for sample S7 may probably be due to the presence of the mineral goethite which is known to shift IEP toward higher values [28].

The absence of IEP in sample S9 may suggest the inability of developed variable charges to compensate the structural negative charges due to the dominance of the latter surface charges [29]. These structural charges originate from isomorphic substitution or crystal imperfections. This implies that the ζ characteristics of S9 have a dual behavior. These are permanent charges which are independent of the surrounding solution and that which is as a result of pH- dependent charges. The absence of an IEP suggests the existence of high magnitude structural charges while the gradual change in gradient of the zeta potential finger print of sample S9 (Fig. 3c) with diminishing pH confirms the presence of variable charges in the sample (S9).

Protonation reactions occurring on Al-OH and Si-OH groups such as in equations (4) and (5) on the clay mineral kaolinite are presumed to account for the accumulation of positive surface charges in this group.

2) Group-2

The samples in Group-2 (S10 to S16) are mainly composed of quartz, kaolinite, and illite (Fig. 2 *black*). The presence of pyrite (in S10, S15, and S16), feldspar (S13) and goethite (S15 and S16) are few heterogeneities within the group (Table I). Figs 4a and 4b are the representation of the ζ fingerprints of the samples within this group. Like the behavior of samples in Group-1, the absolute negative ζ increased with increasing pH and vice versa. The ζ values reported ranged from +68 mV to -61 mV which is relatively higher than those reported in Group-1.

The accumulation of surface negative and positive charges in Group-2 are also as the result of the combined deprotonation and protonation reactions on silanol and aluminol sites on amphoteric edges and basal sites of the clay minerals; kaolinite and illite. These reactions are shown in equations (2) to (3) and (4) to (5) respectively. Reported IEP within the group is also consistent with that reported in literature. The absence of IEP in samples S10 and S14 is an indication of the dominance of structural charges as explained earlier.

It is noteworthy that, variations in surface positive and negative ζ in samples with goethite and significant amount of organic matter may probably arise from de/protonation reactions involving FeO(OH) [28] and -COOH respectively [30]. Also, the dissolution of Al^{3+} from the crystal lattices of muscovite which is almost a common mineral to all the samples (in both groups) may account for the surface positive potential generation toward low pH. Muscovite is mostly unstable at low pH, as such goes into solution releasing Al^{3+} into solution. Of course, variations in the magnitude of the positive zeta potential are due to variations in the amount of the mineral and the susceptibility or rate of dissolution.

Comparison between groups

The average positive ζ values in group-2 (+43.2mV) is relatively higher than that reported in group-1 which is +13.89 mV. This accords well with the lower charge density contribution from kaolinite compared to that from illite [31, 32]. The comparable negative zeta potential averages from both groups (42mV in Group-2 and 40 mV in Group-1) may be due to the pronounced role of the amphoteric sites on the kaolinite compared to the illite.

Table 1: Pertinent sample physical properties

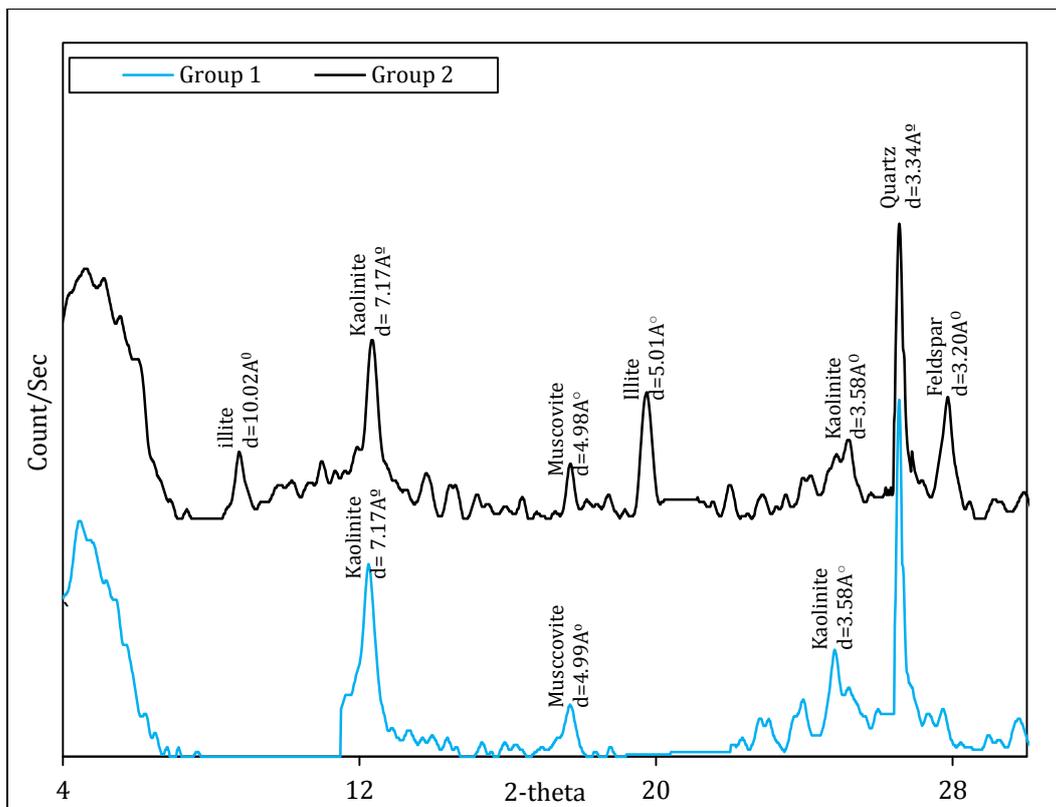| Group ID	Sample ID	Sample Composition From XRD							OM (%)	IEP
		Feldspar	Goethite	Kaolinite	Illite	Quartz	Pyrite	Muscovite		
Group 1	S1			✓		✓		✓	0.50	2.40
	S2			✓		✓		✓	0.86	4.04
	S3	✓		✓		✓		✓	0.99	2.65
	S4			✓		✓		✓	1.06	2.61
	S5			✓		✓		✓	1.19	4.61
	S6			✓		✓			1.22	4.67
	S7		✓	✓		✓			1.23	7.61
	S8			✓		✓		✓	1.26	3.08
	S9			✓		✓	✓	✓	1.32	*
Group 2	S10			✓	✓	✓	✓	✓	1.46	*
	S11			✓	✓	✓		✓	1.47	3.62
	S12			✓	✓	✓			1.58	3.89
	S13	✓		✓	✓	✓			2.13	5.48
	S14			✓	✓	✓		✓	2.82	*
	S15		✓	✓	✓	✓	✓	✓	6.20	4.87
	S16		✓	✓	✓	✓	✓		16.60	7.92

*No IEP

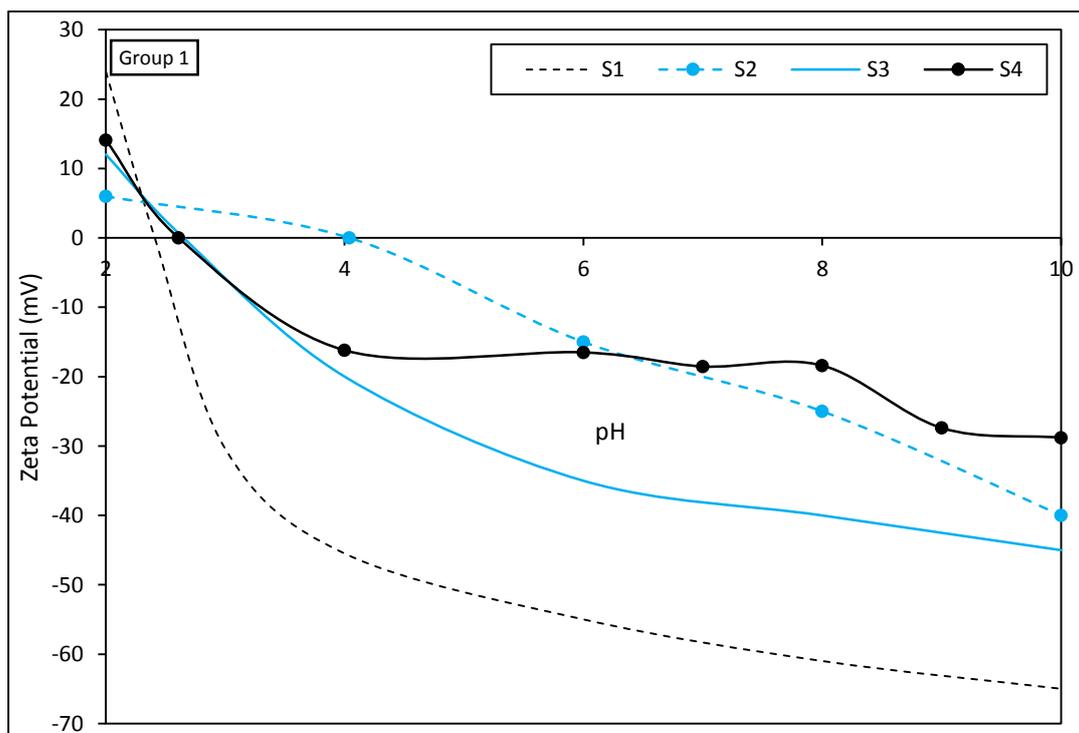**Figure 2:** XRD representative profiles of sample groups 1 and 2

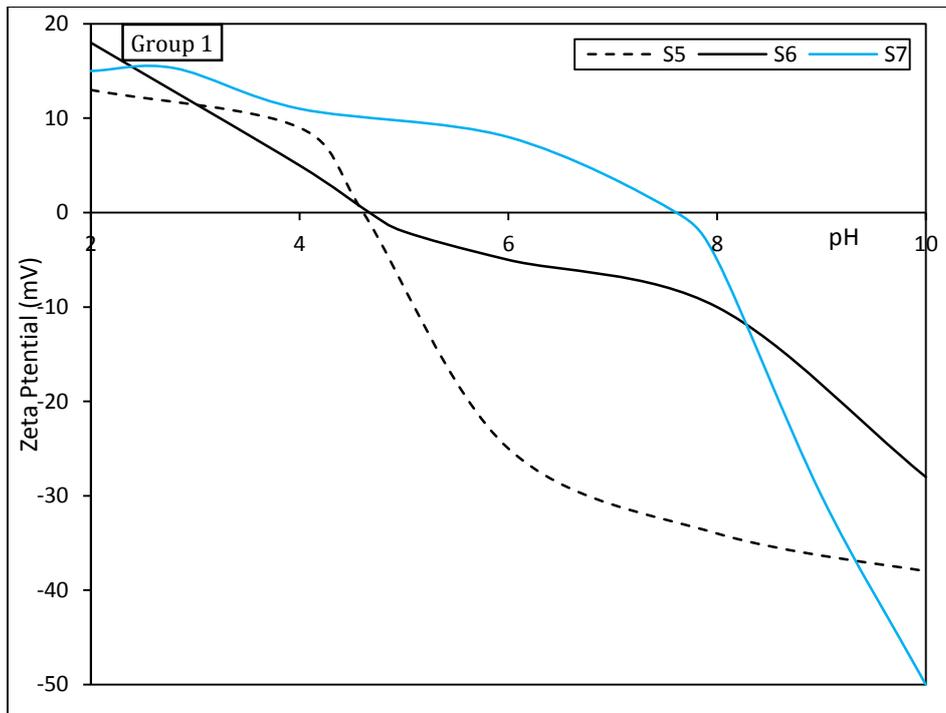**Figure 3a:** Zeta potential profiles of samples S1 to S4 of Group-1 as a function of pH.

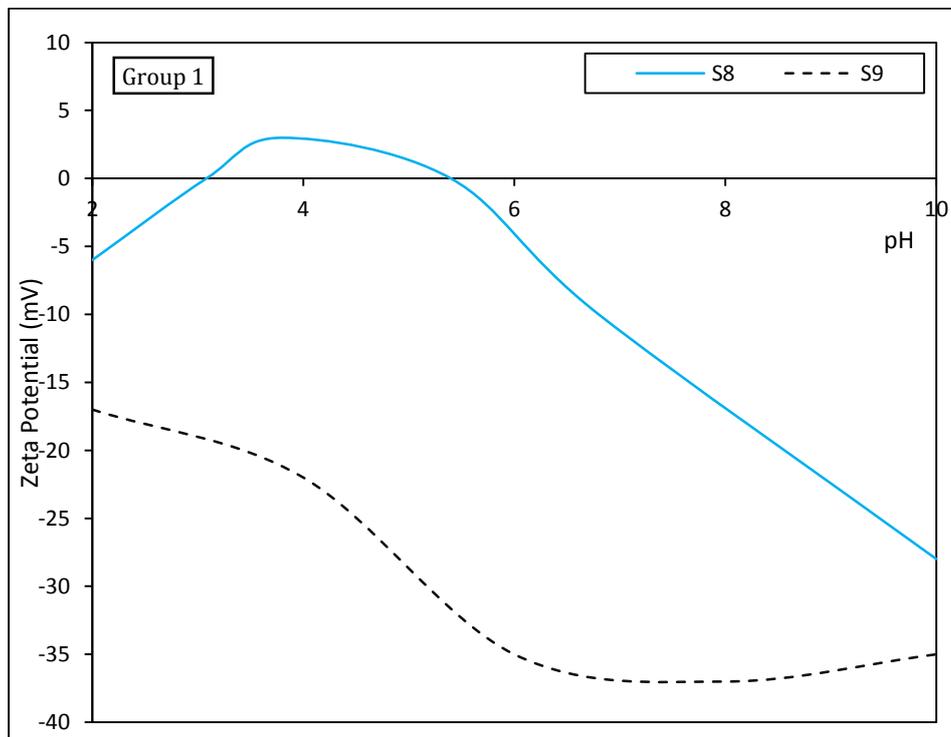**Figure 3b:** Zeta potential profiles of samples S5 to S7 of Group-1 as a function of pH.

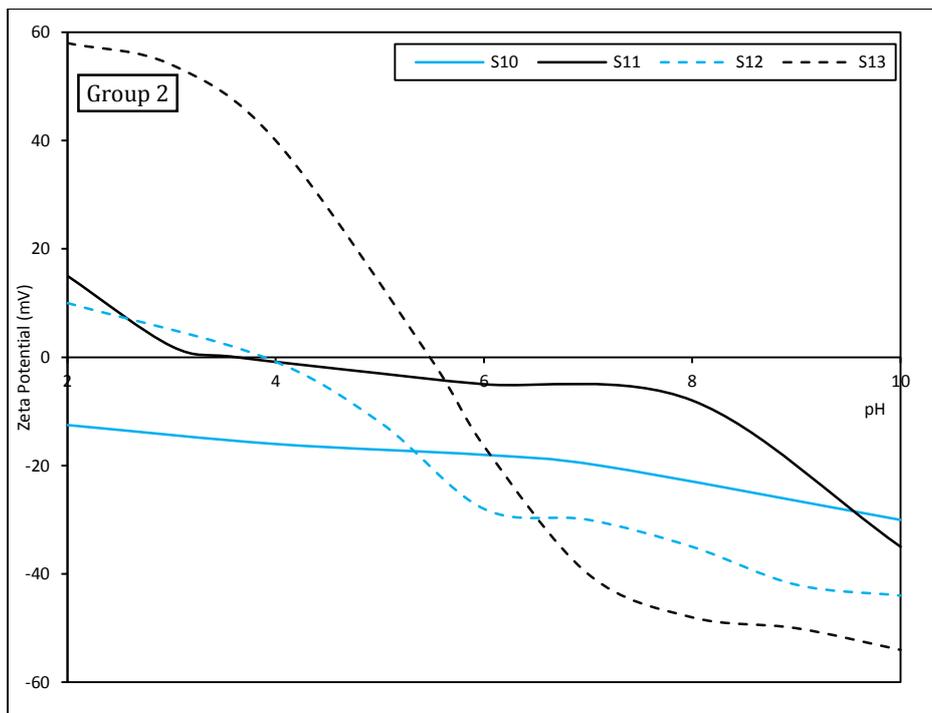**Figure 3c:** Zeta Potential Profiles of samples S8 to S9 of Group-1 as a function of pH

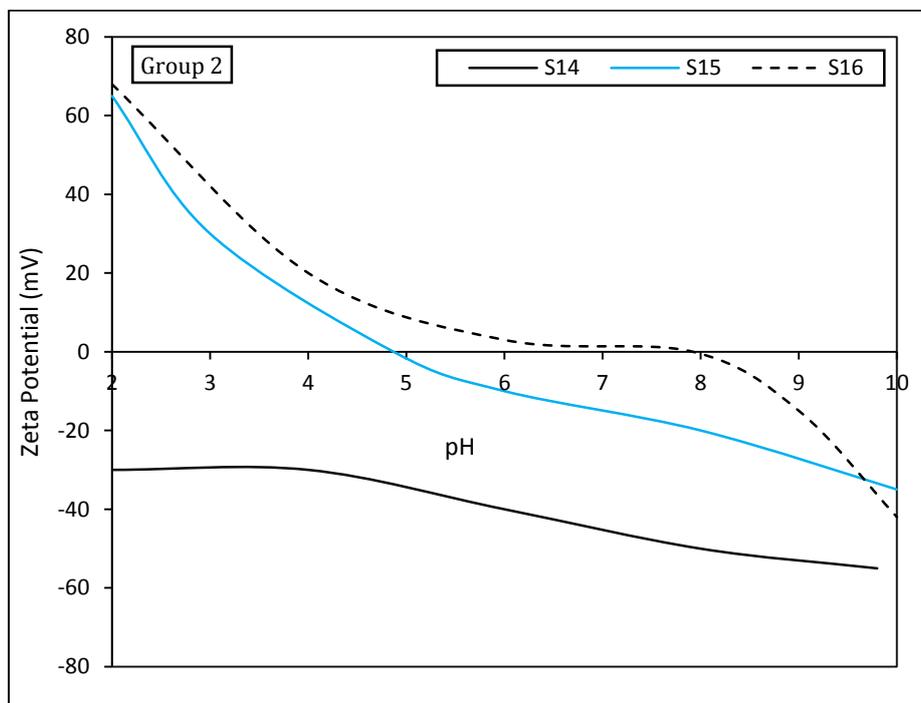**Figure 4A:** Zeta potential profiles of samples S10 to S13 of Group-2 as a function of pH.

Figure 4b: Zeta potential profiles of samples S14 toS16 of Group-2 as a function of pH.

CONCLUSIONS

The study of the zeta potential characteristics of the shale samples from the Setap Formation (Sarawak, Malaysia) has shown that, their surface potential range from +68 mV to -65 mV. Variations in the surface charges in the samples were attributed to variations in clay mineralogy and organic matter content. The former was mainly kaolinite and illite. Kaolinite was the commonest and major phase while illite occurred in some samples. On this basis, the samples were grouped into two. Surface negative and positive charges in the samples with only kaolinite (Group-1) were relatively smaller in absolute values as compared to those samples with both kaolinite and illite (Group-

2). Average negative and positive zeta potentials in Group-1 and Group-2 are -40.02 mV /+13.89 mV and -42.0 mV /+43.2 mV respectively.

Negative and positive surface potentials were ascribed to protonation and deprotonation reactions on Al-OH and Si-OH sites on the edges of kaolinites in Group-1, while a contribution from amphoteric edges of the clay mineral illite was considered for the second group.

Dissociation reactions involving FeO (OH) and –COOH may also have accounted for some surface charges in samples with significant amounts of goethite and organic matter.
An increase of pH with a corresponding increase in surface negative charges observed in all the samples is an indication that ion exchange in the samples can be managed.
A contribution from surface permanent charges also accounted for some surface negative charges. All samples but three reported IEP. The average IEP for the samples is ~4.69, which is typical of kaolinite rich samples.

Samples that reported no IEP were due to the dominance of structural charges that could not be compensated for by positive amphoteric charges. 18.75% of the samples showed this behavior.

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