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VARIATIONS IN SURFACE POTENTIAL CHARACTERISTICS OF SELECTED SHALES FROM CENTRAL LUCONIA, OFFSHORE SARAWAK- MALAYSIA

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Abstract

Surface potential measurements deduced from electrophoretic mobility were made on organic shale from the potential source rocks from Central Luconia, offshore Sarawak basin, Malaysia, with the aim of determining the ionic binding properties of the rocks. Variations in zeta potential were attributed to protonation and deprotonation reactions occurring on amphoteric sites (Al-OH and Si-OH) of kaolinite, which is the dominant clay mineral phase among the shales. Dissolution of Al^{3+} from the crystal lattices of muscovite and contribution from illite were also considered as surface potential variants in specific samples. The influence of shale chemical composition and organic matter content on surface charge characteristics was studied by correlating results from total organic content analyses, X-ray fluorescence spectroscopy, and isoelectric points. Organic matter showed no relationship with isoelectric points, but an enhancement of isoelectric points was observed with increasing Al_2O_3 and Si/Al ratios.

Keywords: *Isoelectric Point; Kaolinite; Organic Matter; Shale; Zeta Potent.*

1. Introduction

Zeta potential (ζ) 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 (Figure 1) of charged particles [2]. The sign of these measurable electric data is similar to that of excess charge 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] so that only a brief background is given here.

Generally, particulate shales possess surface charges generated through mechanisms such as differential ion adsorption from the electrolyte solution, differential ion dissolution from a crystal lattice, surface anisotropy, isomorphous substitution and ionization of surface functional groups; the so-called Nernst potential. The degree of surface potential generation is known to be dependent, to a greater degree, on solution conductivity, electrolyte concentration, and pH, but it seems that the effect of pH is mostly the subject of scientific discussion [6]. The dependence of surface potential on solution pH is important for the present study because shales are composed of admixtures of clay minerals that bear surface variable charges.

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 this charge distribution influence is termed the electric double layer (EDL) [2-3]. The EDL consists of an inner stern layer and an outer diffuse layer. Particle movement in solution due to an applied voltage causes 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; zeta potential is the subject of interest in this research.
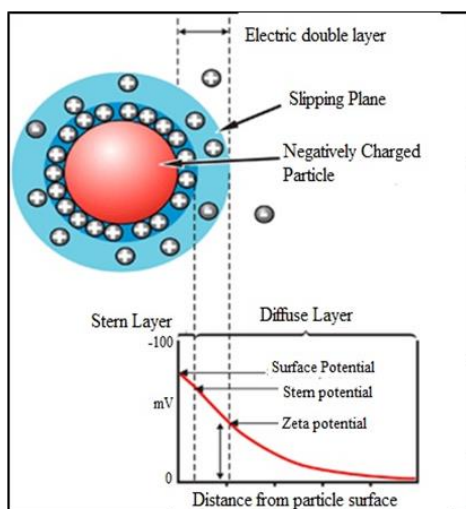
Figure 1. Schematic Representation of EDL and ζ modified after [4-5]

The measured magnitude of zeta potential is a good index of the magnitude of electrostatic repulsive interaction between shale particles as such can be used to predict and control the stability of the shale particles in dispersion [7]. Generally, the dividing line between stable and unstable suspensions is generally within the range of +30 mV ≥ ζ ≥ -30 mV. All particles that fall outside this range are considered stable. The point of least stability is when ζ is zero, and the pH of occurrence is termed the isoelectric point (IEP) [7]. ζ is mostly deduced from electrophoretic mobility (EM) [7]. Besides its experimental accessibility, the parameter is known to be intricately related to many geological processes. Zeta potentials do not only influence organic matter (OM) accumulation in source rocks [9-10], but their interactions in aqueous solutions control gas adsorption and fluid flow rate [11] through reservoirs. Thus, as it is also well-known, the zeta potential is the most important factor controlling the distribution of hydrocarbons in pores [12].

The zeta potential of shale particles is seldom well-defined. The heterogeneities in surface potential in aqueous media are caused by complexities in the crystal structures and chemical composition of the mineralogical components of the shale. Foreign surface-bound materials such as organic matter can be an additional source of heterogeneities to surface potential. The layered silicates also account for most variable surface potential in shales [13] due to the presence of charges on their lamellae [6,14-15]. Measured surface potential due to clay minerals in shale is mostly high in magnitude as compared to that from other reservoir rocks such as coarse siliciclastics and carbonate materials, which might probably explain the occurrence of large quantities of hydrocarbon as 'sorbed gas' in unconventional shale settings [16-21]. The type of clay mineral present has also been pointed out to be a major influence on the sign and magnitude measured in the shale particles.

El-Swaify [22] and later Nmegbu and Spiff [23] 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 is known to govern important properties such as adsorption, flocculation, coagulation and aggregation [6, 24] a brilliant idea which has been successively exploited and applied in effective hydrocarbon evaluation [12] and oil gangalia displacement (Sensu Gu et al. [25] and Nmegbu and Spiff [23]). 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 [26-27].

Although all these aspects are well documented and published, no paper deals with the zeta potential generated on the surfaces of shales from Central Luconia of the Sarawak basin of Malaysia. In this regard, this study is aimed at characterizing and determining the variations of the zeta potential generated by selected shales from Central Luconia.

2. Materials and methods

Powders of five onshore samples labelled CL1 to CL5 from offshore Central Luconia (Cycle III) were used for the study. Samples were recovered from well named "E15-1" E at shaly intervals in an otherwise carbonate succession.

Mineralogical compositions were derived from X-ray diffraction (XRD) patterns measured on randomly oriented powders. Analyses were performed on the fine fraction from representative shale samples of uniform crystallite sizes achieved through milling with a Fristch - Pulveristte 2 mill and procedures detailed by Macedo and Bryant [28]. Diffractograms were recorded in the 2θ in the range of 3° to 60° with a scan speed of 1°20/mm. All reported mineral compositions relate to the crystalline content of the analyzed samples. Fourier Transform Infrared (FTIR) spectroscopy was achieved on an Agilent Technologies Cary 660 Series FTIR Spectrometer. Samples of 2 mg and 0.5 mg were dispersed in PIKE MIRACLE diamond attenuated total reflectance spectroscopy (ATR) to record optimal spectra in the regions of 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans. Mineral morphologies were determined by Field Emission Scanning Electron Microscopy (FESEM).

The chemical composition of the shales was determined by X-ray fluorescence (XRF) spectroscopy using a Bruker S8 Tiger wavelength dispersive X-ray fluorescence spectrometer. Total organic carbon (TOC) was determined on bulk and fractionated sediment samples using an Analytikjena carbon analyser.

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

$$\zeta = \frac{4\pi V}{\varepsilon} \text{ EM} \qquad\qquad (1) \text{ [29]}$$

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 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). Values of pH of dilute dispersions were determined directly and adjusted with HCl and KOH between 2 < pH < 10 before the introduction of samples into the capillary cell. A titration unit in the Surpass^{TM} electrophoretic measuring system, which adjusted the pH of the sample suspension to pre-programmed values and to selected rates of titration, made isoelectric (IEP) identification possible with commensurate precision with a single sample.

3. Results and discussion

A summary of results from XRF, TOC and zeta potential analysis of the five samples are presented in Table 1. Sample mineralogy after XRD, and ATR-FTIR analyses are presented in Table 2. Figures 2a-e give a visual representation of each sample mineralogy in FESEM micro-graphs. Sample values of SiO_2 and Al_2O_3 are indicated in Figure 3.

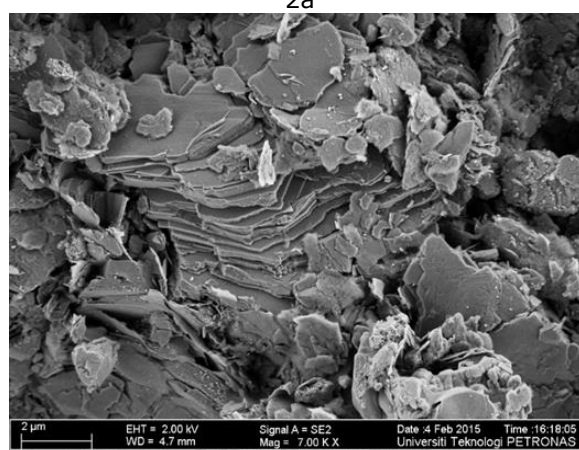Table 1. Chemical composition and pertinent physical properties of shale samples

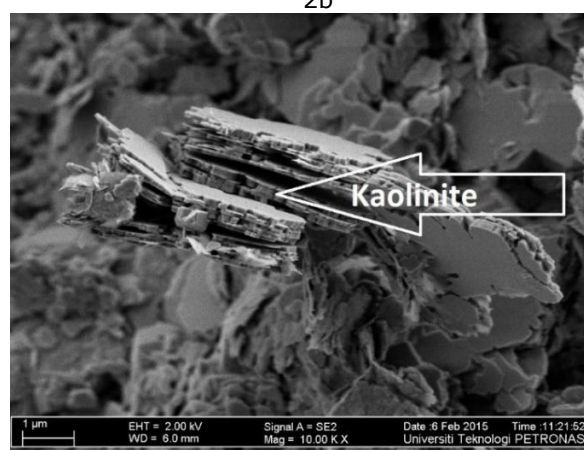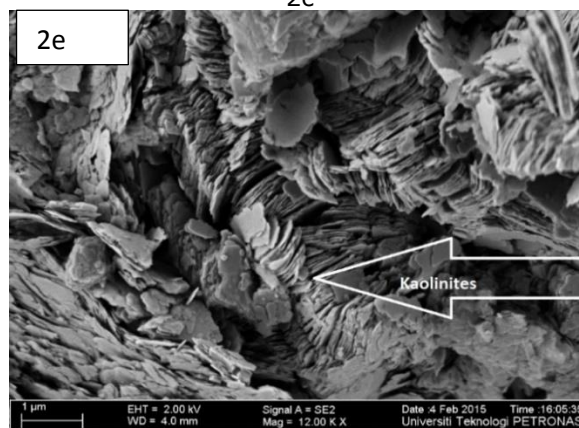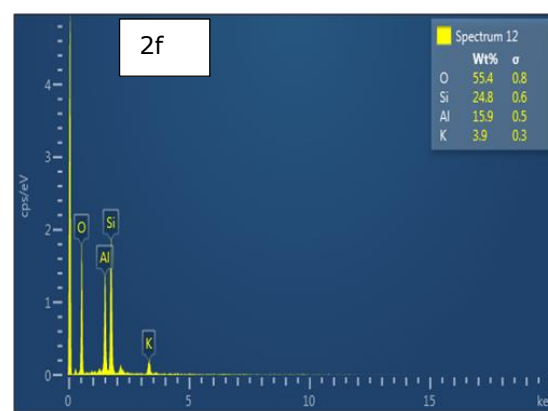| Sample ID	Sample composition after XRF			TOC (%)	IEP
	SiO_2 (%)	Al_2O_3 (%)	SiO_2:Al_2O_3		
CL1	52.31	18.10	0.3480	0.47	5.47
CL2	54.60	18.50	0.3388	0.72	3.10
CL3	51.80	17.90	0.3456	2.36	5.05
CL4	51.40	17.80	0.3463	0.94	4.18
CL5	51.20	18.05	0.3525	0.67	5.60
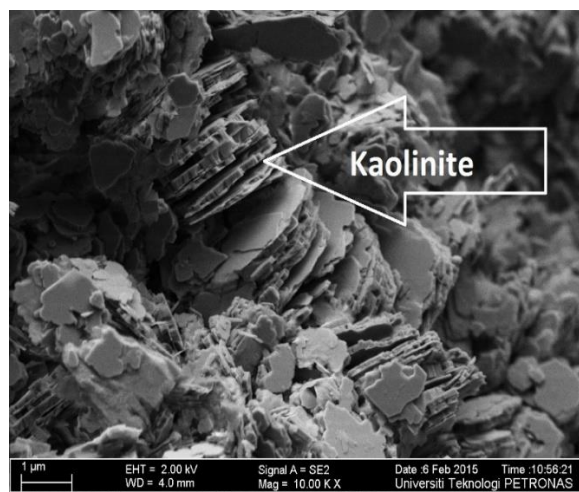
2a
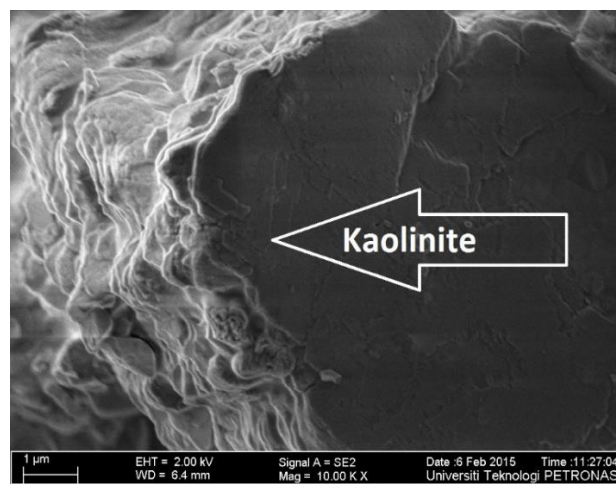
2b

2c

2d

2e

2f

Figures (2a-e) FESEM micrographs showing the dominance of the clay mineral kaolinite in samples C1 to C5. (2f): Representative EDS spectra of the dominant clay mineral in the studied samples

Table 2. Summary of mineralogical results after XRD and ATR-FTIR

| Sample ID	Illite	Kaolinite	Muscovite	Quartz
CL1		✔	✔	✔
CL2		✔	✔	✔
CL3	✔	✔		✔
CL4		✔	✔	✔
CL5		✔	✔	✔
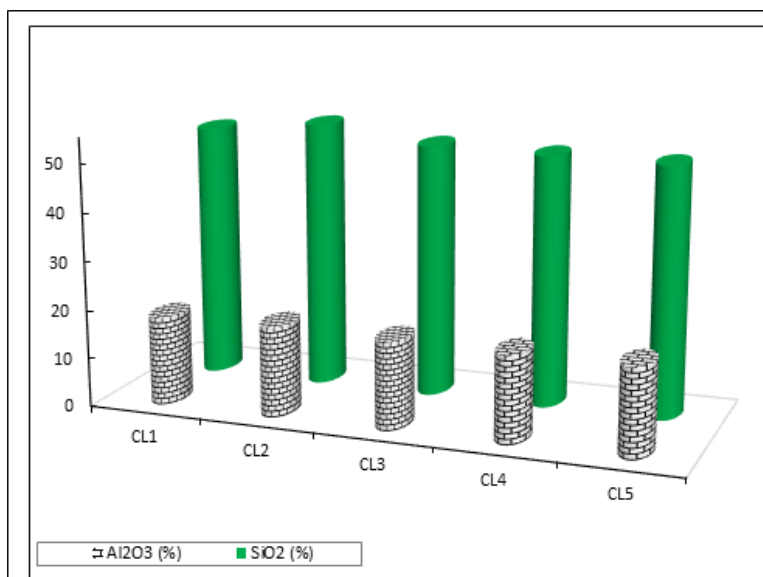
Figure 3. Distribution of Al_2O_3 and SiO_2 in the shale samples

3.1. Mineralogy

The mineralogical composition of all five samples is fairly uniform and composed of quartz and clay minerals. Among the latter, the presence of kaolinite is the majority in all samples, followed by muscovite/illite (Table 1). The dominance of kaolinite as the major clay mineral phase is concluded after the intensity readings of XRD and FTIR peaks. This is confirmed by visual observations on FESEM micrographs (Figures 2a to 2e).

3.2. Chemical composition

Geochemically, the SiO_2 content of the shales range from 51.20% to 54.60%, with an average of 52.26% (Figure 3). Thus the average SiO_2 in the shales studied herein is below that given by Pettijohn [30] (58.50%) and Gromet et al. [31] (64.82%). Al_2O_3 concentrations are within the range of 17.80% and 18.50%. Sample CL2 reported the highest percentage of Al_2O_3, while CL4 reported the least (Table 2; Figure 3). The average Al_2O_3 concentration in the studied Central Luconia shale samples under investigation is relatively higher than that reported by both Pettijohn [30] and Gromet, et al. [31], which are 15.40% and 17.05% respectively.
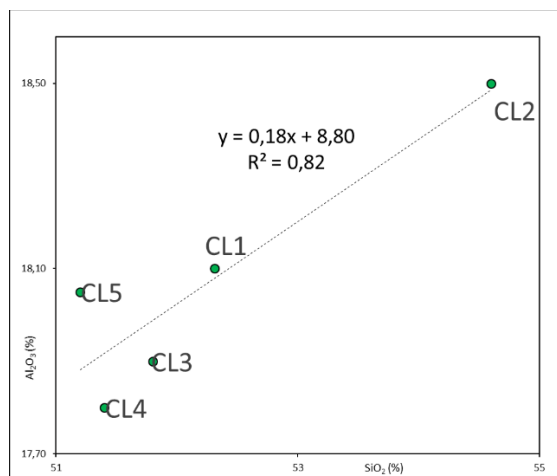
Figure 4. Relationship between SiO_2 and Al_2O_3 in the samples

Obviously, after Table 2, SiO_2 is the most abundant chemical constituent of the studied Central Luconia shale samples, which is consistent with the work by Gromet et al. [31]. In general, according to Pettijohn [30], SiO_2 exists in shales as a part of clay minerals, as undecomposed detrital silicates and as free silica. Al_2O_3, like SiO_2, may also exist either as a part of clay minerals or as free aluminium hydroxide minerals (e.g., gibbsite). However, in this study, the strong positive correlation ($R^2 = 0.82$) between SiO_2 and Al_2O_3 (Figure 4) is a strong indicator that these major oxides are associated with the aluminosilicates [32]. This is consistent with the occurrence of clay minerals identified by XRD, FTIR, and FESEM (Figure 2a to 2e) analyses, among which kaolinite is the dominant phase.

3.3. Electrochemistry-Zeta potential

Zeta potential (ζ) values have been estimated from the five shale samples after the electro-phoretic mobility, using the equation (1) over a pH range of 2 to 10. Those values have been used to characterize the development of surface potential on amphoteric sites on mineral con-stituents. Values are represented as a function of pH in Figures 5a-b. Marked changes in the development of ζ were observed in all the shales as a function of pH, with absolute negative ζ decreasing with decreasing suspension pH. The reverse is true for basic conditions. Zeta potential (ζ) reported in the shales is within the range of +37 mV to -30 mV. The average positive and negative ζ reported for the five samples are +25.51 mV and -17.6 mV respect-tively. Samples CL2 and CL5 reported the least negative ζ (-10 mV). The highest positive zeta potential of +37 mV was recorded in sample CL3 (Figure 5a). The zeta potential values presented herein are within the range of values reported for shale in the literature [33-34].

All the samples reported a distinguished pH identified as the isoelectric point (IEP) where the measured ζ recorded in the shale equals to zero. The range of IEP measured in the samples is between 3.10 and 5.60. The lowest and highest IEP were measured in samples CL2 and CL5 respectively. An average IEP of 4.68 is herein calculated for the shale.

The dependence of ζ-generation on pH is often attributed to the protonation and deprotonation of potential-determining ions on the surfaces of organic matter [35] and mineral surfaces [36-37].
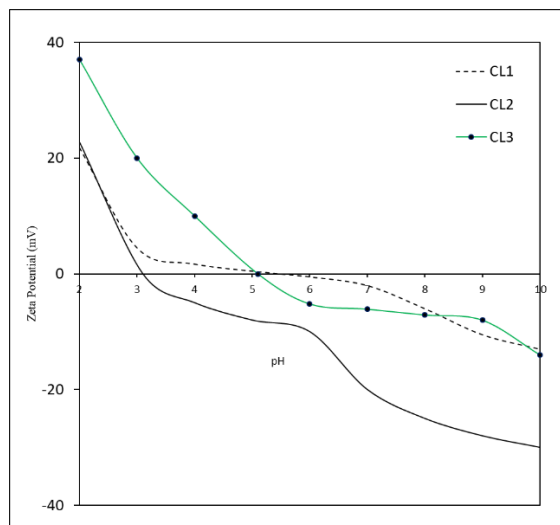

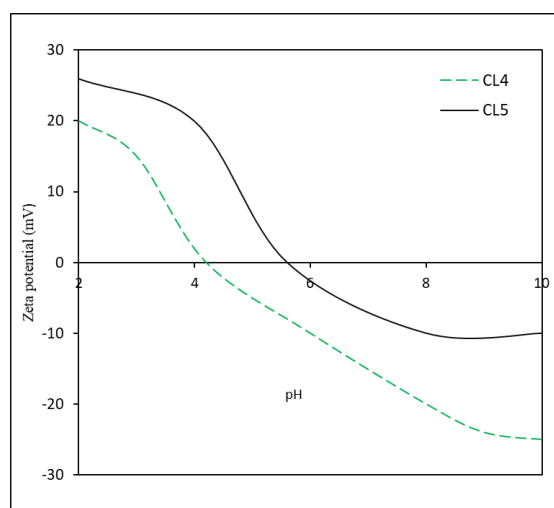Figure 5a. ζ of CL1 to CL3 as a function of pH   Figure 5b. ζ of CL4 and CL5 as a function of pH

For geological materials that differ remarkably by mainly organic matter content (Table 2), Wada and Okamura [35] showed that protonation and dissociation reactions involving carboxylic (-COOH) functional groups such as those presented in equations (2) and (3) respectively account for variations in the zeta potential.

$$-COO\text{-}H \longleftrightarrow -COO^- + H^+ \quad (2)$$
$$-COOH + H^+ \longleftrightarrow -COOH^{2+} \quad (3)[35]$$
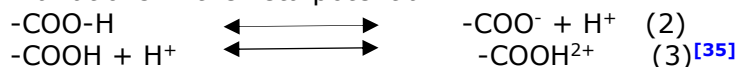
Although protonation constants of –COOH functional groups are mostly greater than 4 (thus incapable of such acidic IEP values reported in Table 1), it is however possible for complex multifunctional macro-molecules like shale organic matter to interact with neighbouring sites which may alter dissociation constants and account for low IEP values like those reported in this study (Table 2)[38].
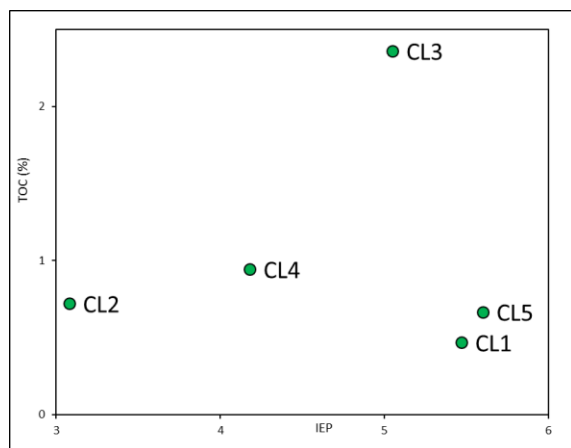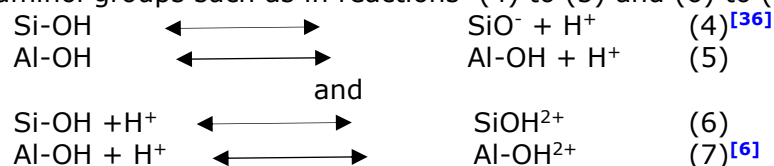
Figure 6. Relationship between of TOC (%) and IEP

Organic matter has been suggested by numerous authors to lower IEP [39-41]. Others like Fox [42] , Appel *et al.* [43] and Fosu-Duah [34], and Fosu-Duah *et al.* [44] have also reported a positive correlation between TOC and IEP. Although the influence of the amount of organic matter present is clearly known to materially affect the development of ζ in geological materials, it is irrelevant to this study. This is supported by the lack of correlation between the two para-meters as shown in the scatter plot in Figure 6.

The ζ and acidic IEP values of the shales may, therefore, be a reflection of the silicic mineral composition of the shales such as quartz, muscovite/illite and kaolinite (Table 2).

These minerals have characteristically acidic IEP values [39,43]. However, in terms of surface chemistry, aluminosilicates are the most reactive mineral constituents of shales [45], given that deprotonation and protonation of H^+ and OH^- are likely to occur on the amphoteric sites of the clays [46].

According to Parks [47], Tombácz and Szekeres [36] and then Eslinger and Pevear [48], negative and positive charges in geological materials arise from the significant contribution of amphoteric edges and basal (OH) (O face) sites through deprotonation and protonation from silanol and aluminol groups such as in reactions (4) to (5) and (6) to (7).

$$Si\text{-}OH \longleftrightarrow SiO^- + H^+ \qquad (4)^{[36]}$$
$$Al\text{-}OH \longleftrightarrow Al\text{-}OH + H^+ \qquad (5)$$

and

$$Si\text{-}OH + H^+ \longleftrightarrow SiOH^{2+} \qquad (6)$$
$$Al\text{-}OH + H^+ \longleftrightarrow Al\text{-}OH^{2+} \qquad (7)^{[6]}$$

Various heterogeneities like the type of clay mineral and concentration account for variations in the magnitude of the zeta potential recorded in the samples. Since kaolinite is the major clay phase in the shale, it is likely that the surface electrical reactions are dominated by protonation and dissociation reactions which occur on the surfaces of this clay mineral. It is also noteworthy to mention that, dissolution of Al^{3+} from the crystal lattices of muscovite and/or a contribution from the silanol and aluminol groups of illite may also account for some variations in the zeta potential of these samples.

3.03.1 Isoelectric points (IEP)

Heterogeneous geological material like shale must have a reflection of its mineralogical suite on the zeta potential properties such as IEP. Several studies have demonstrated this using binary system (silicon-aluminium; [47]) and can be extrapolated to multicomponent mixtures [34]. Recalling from Table 2, the IEPs reported for the samples seem to fall within the range of values mostly assigned in literature to kaolinitic samples [34,43,50]. This may support the earlier suggestion that kaolinite which is the commonest and abundant clay mineral in the studied shales are probably the main variant of zeta potential properties. On the basis of mineralogical composition, Parks [51] suggested that the IEP can be predicted semi quanti-tatively proceeding from simple oxides. For example, aluminosilicates like kaolinite should have an intermediate IEP value between that of pure Al_2O_3 and SiO_2, the particular IEP value being dependent on the Si/Al ratio given. This implies that the IEP of each shale is the weighted average of the chemical components' isoelectric points [33,51].

In this study, the relatively low IEP (3.10) of sample CL2 may, therefore, be a reflection of the relatively low $SiO_2:Al_2O_3$ ratio reported (Table 2). Nevertheless, deviations from the norm can also be found. For instance, sample CL3, when compared against CL4, shows an

unexpected lower $SiO_2:Al_2O_3$ ratio (0.3456 vs. 0.3463) and a higher IEP (5.05 vs. 4.18). This discrepancy may, however, point to factors other than just the $SiO_2:Al_2O_3$ ratio.Hu and Liu [52], Hu et al. [53] and Miller, et al. [15] suggested that heterogeneities of the structural layers of clay minerals significantly affect the surface zeta potential characteristics. Although the IEPs of CL1, CL3, CL4 and CL5 (Table 2) are within the acidic range, these values suggest the pronounced contribution of the aluminol components of the shale; most of these components might be due to kaolinite, which is the major clay phase in the shale. This is supported by the positive correlation (R^2 = 0.81) between IEP and Al_2O_3 (Figure 7). (Recalling from the geo-chemical analyses, Al_2O_3 is shown to be mainly associated with the clay mineral constituents; Figure 4).

An increase in the $SiO_2:Al_2O_3$ ratio has been shown to be positively correlated with IEP in many publications [15,34,52,54 but there is still a controversy on the ability of the aluminol components of clays to shift IEP values from those of pure clays into higher ones, and the conditions at which this occurs [55-56]. For instance, the works of Angove et al. [50], Hu and Liu [52], Miller et al. [15] and, Gupta [29 support the positive correlation between $SiO_2:Al_2O_3$ ratio and IEP values, in very much the same way as we found in this study (R^2 = 0.81, Figure 8). However, the conclusions of Miller et al. [15] and Hu and Liu [52] that the aluminol components of aluminosilicates have insignificant influence on their surface charge characteristics – even though there is an equivalent exposure of both silanol and aluminol sheets, especially in kaolinite – contradicts that of Angove et al. [56] who reported an IEP value of 7.3 for pure kaolinite. An explanation for this contradiction was given by Gupta [29], who claimed that the technique of deducing zeta potentials from electrophoretic mobility is mostly compromised by the heterogeneities shown by the clay minerals.
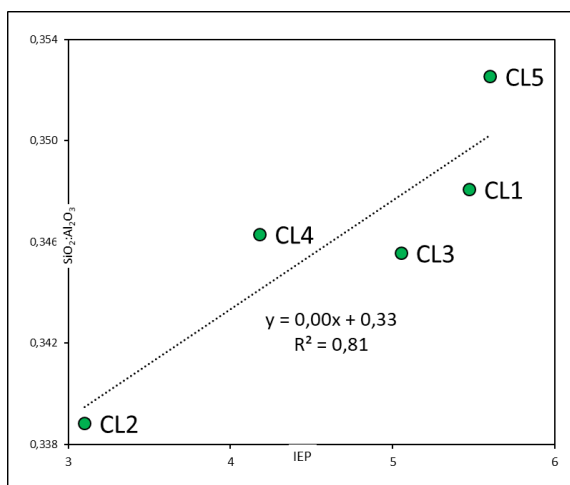

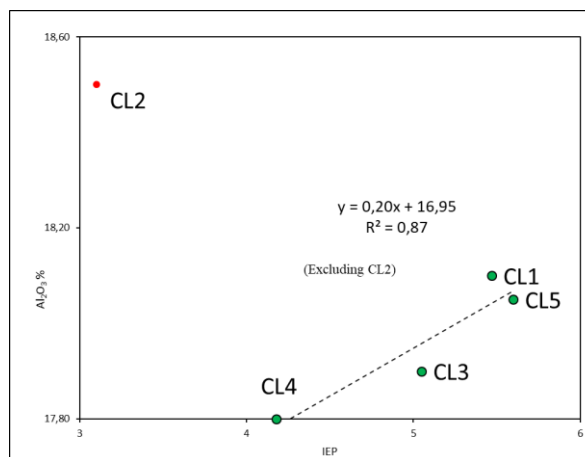Figure 7. Relationship between $SiO_2:Al_2O_3$ and IEP

Figure 8. Relationship between Al_2O_3 (%) and IEP

In this study, the positive correlation between four of the samples (R^2 = 0.87; excluding sample CL2 Figure 8) suggests that the amount of Al_2O_3 has a significant influence on the surface potential of the Central Luconia shale. This might explain the relatively high IEPs of CL1, CL3 and CL5 (Table 2) which are closer to that of pure Al_2O_3 (IEP~8, [57]. It may also suggest an equal contribution of SiO_2 and Al_2O_3 to the surface charge characteristics of the shale despite the relatively high percentages of the former. If this is true, then IEP of samples CL1, CL3 and CL5 are thus equal to the mean of the IEPs of pure SiO_2 (~3) and Al_2O_3 (~8) which is ~5.5 (similar to those reported for CL1, CL3 and CL5 in Table 2), which is consistent with the work by Parks [47].

4. Conclusions

The study of the surface charge characteristics has shown that zeta potential (ζ) gene-rations in Central Luconia on the average range from +25.51 mV to -17.6 mV. An average IEP of 4.68 has been assigned to the shale.

- The influence of organic matter on surface charge characteristics is insignificant. Shale chemical composition is the main variants of surface potential specifically the activities on the amphoteric sites of clay minerals.
- The gradual change in the magnitude of the zeta potential observed as a function of pH is a good indication that the expulsion and sorption capacities of the shale can be managed.

The relatively high average positive zeta potential of the shales in comparison with the negative zeta potential indicates that the shale have high anion sorption capacities.

Acknowledgements

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