

Electrophoretic Behavior of Some Shales from the Setap Formation, Sarawak Basin, Malaysia

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Abstract

Electrophoretic mobility has been used to investigate the surface potential characteristics of six shale samples from the Setap Formation of the Sarawak basin-Malaysia. The zeta potential ranged between +80 and -80 mV. Apart from one sample that remained electronegative throughout the entire pH range of this investigation, all the samples exhibited isoelectric points (IEP). The four of the IEP values were in the acidic range (2.4-3.62) which is characteristic of kaolinite rich colloids. The relatively high IEP of 7.92 reported by one of the samples was attributed to the shift by the mineral oxidic minerals (goethite) toward higher values. Further data analysis done outside the scope of the objectives of this study revealed a positive correlation between Fe_2O_3 and IEP with correlation coefficient of 0.82. This supports well-published relationships between the two parameters. The behaviour of the surface potential properties in the Setap Formation is an indication of variabilities in its sorption capacities.

Keywords: Electrophoresis, Iron Oxide, Isoelectric Point, Shale, Zeta Potential.

Introduction

The surface potential or charge properties of shales play peremptory role in determining several properties of major geological ramification in aqueous solution. Surface potential is as a result of interfacial interaction with sorptives (fluid-rock) caused by electrostatic driving forces. This implies that, oppositely charged ions sorbs on charged surfaces [1] [2]. No meaningful study of adsorption in shales can ever be imagined without the consideration of the ion-binding properties of the shales. In a labyrinthine, surface charge characteristics are intricately connected to almost all processes in the petroleum cycle [3].

Not only do the charge properties influence organic matter accumulation in source rocks [4][5], their interactions in aqueous solutions control gas adsorption [6], fluid flow rate

[7] through reservoirs and are also known to be the single most contributing factor controlling distribution of fluids in pore spaces [7]. More importantly, surface charges are known as the primary dictator of the recovery rates of reservoirs [8][9]. Shale's high surface potential density also, have over the years be shown to account for its higher storage capacity as compared to other reservoir rocks with equivalent pore volume [6][10][11].

In addition, the physicochemical and charge properties of particles are inextricably related, for the sign and magnitude govern important properties such as flocculation, coagulation and aggregation [12][13]. For example, maintaining the physicochemical properties of shales as flocs is essential for processes such as Microbial Enhanced Oil Recovery (MOER) in reservoirs [12]. (MOER is a group of phenomena which target ganglia of residual hydrocarbons entrapped by capillary forces and surface potential properties of reservoir rocks by using nontoxic excreta of microbes causing physical changes (flocs) in the crude thereby enhancing the amount of oil produced [12]).

The sign and magnitude of surface potential of shale particles can be conveniently be described using the isoelectric point (IEP)[14][15][16]. The IEP refers to the pH at which the value of the net variable surface charge component of the shales particles is zero [15][17][18][19]. Colloidal particles are least stable at the IEP. All pH values above the IEP will result in a net negative surface potential while acidic conditions will result in positive shale particle colloids [2][14]. This imply that the former will exhibit a cation exchange capacity while an anion exchange capacity will be true for the later. Generally, most colloids including shales are negative at near neutral pH [1]. IEP is a physical property controlled by mineralogy and other factors such as oxide and organic matter content [14][20][21]. It is related to sample constituents and does not vary by external factors such as water content, time, location, etc. IEP thus is an important parameter that can be considered intrinsic. It can therefore play decisive role in shale physicochemical characterization [14].

The IEP of pure minerals such as kaolinites and goethites are well defined but the heterogeneous nature of shales will result in the formation of a continuum of IEPs. This is because, the IEP of the shale will be the mean of the IEPs of all the minerals that make up the shale. For example, at pH greater than (>) 2.4 a shale possessing only kaolinite and goethite would have positively charged goethite surfaces and negatively charged kaolinite surfaces. Depending on the kaolinite-goethite ratio, the IEP of such a shale can at least be semi-quantitatively predicted to be in between that of kaolinite (~3) and goethite (~8) [1][14] [22].

Technically, the IEP of many colloids have been determined by various researchers using a variety of direct methodologies such as potentiometric titration and ion adsorption studies [14][15]. The parameter has also been inferred from maximum sedimentation rates, coagulation kinetic studies and heat of immersion values [5]. These techniques are very common but have well documented associated problems of being laborious and time-consuming [1][14][15][23][24][25]. Also, the focuses of the researchers were mainly on pure minerals and agricultural soils.

For these reasons, this study is therefore aimed at investigating the surface potential properties and evaluating the probable variability in IEP of shales from the Setap Formation using the less frequently used, time-efficient, reliable and reproducible electrophoretic mobility approach recommended by authors such as [26][27][28]. The results will be interpreted against mineralogical variations in the samples.

Materials and Methods

Powders of six (6) shale onshore samples labelled Q1-Q6 from the Setap Formation were used for the study.

A. Geological Setting

The study areas are located in the Sarawak basin of Malaysia. The basin is a highly proven prolific basin which presently is the main contributor to hydrocarbon production in the country [29]. The details on the tectonics of the Sarawak basin and sedimentation of the Setap Formation are given in [29] [30][31].

B. Mineralogical and Chemical Analysis

Sample mineralogical composition was determined from X-ray diffraction (XRD) patterns measured on randomly oriented powders. Analyses were performed on the fine fraction from representative samples. Using a scan speed of 1°20/mm, diffractograms were reported within the range of 3°- 60° (2θ).

The chemical composition was determined by means of an X-ray fluorescence analyses using a Bruker S8 Tiger wavelength dispersive X-ray fluorescence spectrometer.

C. Electrophoretic Measurement

The electrokinetic properties of the samples were determined with an Anton Paar Surpass™ Electrokinetic Analyzer (SEA) at 25 ± 0.1 °C equipped with an attract software which automatically converts electrophoretic mobility of particles to zeta potential (ζ) using the Helmholtz-Smoluchowski equation [32][33].

Stock dispersions were diluted to ~0.05 g/l solid content and the salt concentration of dilute systems were adjusted to a constant concentration of KCl (0.001M). Values of pH for 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™ electrophoretic measuring system which adjusts the pH of the sample suspension to pre-programmed values, and to selected rates of titration made isoelectric point (IEP) identification possible with commensurate precision using a single sample.

Results and Discussion

A summary of results from XRF and IEP from ζ analyses are presented in Table 1. Fig 1 represents the XRD spectra of the six samples (Q1-Q6).

TABLE.1. Pertinent Properties of Shales

Sample ID	Oxide composition after XRF	IEP
	Fe ₂ O ₃ (%)	
Q1	2.85	2.40
Q2	5.40	2.61
Q3	15.40	3.08
Q4	16.50	3.62
Q5	18.87	7.92
Q6	6.00	-

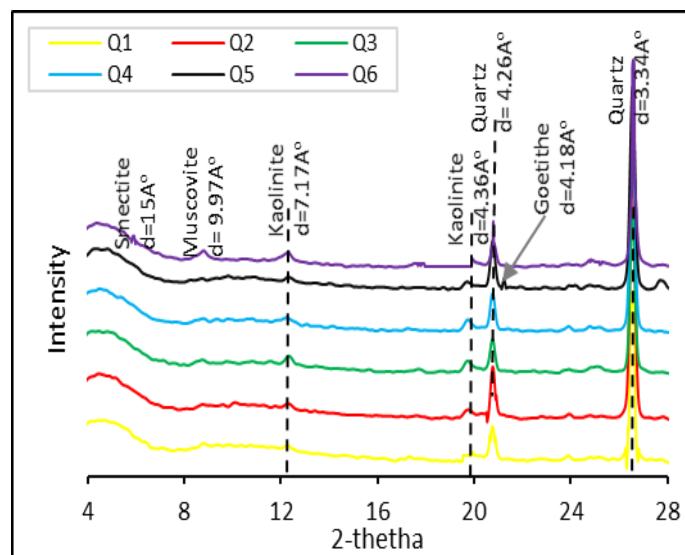


Figure 1: XRD Profile of Studied Samples

A. Mineralogy and Chemical Composition

The study of XRD diffractograms show that, the mineralogical composition of the six samples are fairly homogeneous with kaolinites and quartz as the commonest minerals. The former is the dominant clay mineral in all the samples. Slight heterogeneities however are the presence of goethite in Q5 and smectite and Muscovite in Q6 (Fig. 1). The mineralogy is consisted with those reported by [34].

The chemical composition from XRF show a range of Fe_2O_3 values from 2.85%-18.87% (Table 1). Samples Q1 and Q5 reported the least and highest Fe_2O_3 values respectively.

B. Electrophoretic Mobility

ζ estimation from particle electrophoretic mobility are represented as a function of pH in Fig. 2 and 3 for the samples. ζ values ranged from -80 mV to +80 mV. The electrophoretic mobility behavior of Q1, Q2, Q4, Q5 and Q6 were similar with surface potential reducing from positive at lower pH to more negative values at high pH. The behavior of Q3 however, is slightly different within the pH range of this study. At $\text{pH} > 9$, Q3 exhibited surface net negative charges of -28 mV but shifted to less negative ζ values with pH decrease until about $\text{pH} \sim 3$. Surface negative charges began to shift toward more negative surface charges again below $\text{pH} = 3$ until a net negative ζ of about -58 mV. The abrupt decline of surface potential to negative values with the associated change in the gradient of the curve of Q3 may be attributed to the dissolution of oxides causing depletion of protons at lower pH [35].

The electronegative behavior of Q6 (Fig. 3) throughout the range of pH of this research supports the characteristic naturally electronegative nature of colloidal suspensions [1]. An explanation to such a behavior is probably due to the negligible effect of developed surface variable charges on amphoteric sites of clay surfaces compared to the structural charges that are present at the mineral edges, probably on the smectites which are known to have relatively high negative (absolute value) structural charges. Thus, the generated variable surface potential on amphoteric sites is insignificant to compensate for the net surface permanent charges which explains the absence of an IEP on the sample within the pH range studied.

The other five samples show distinct pH values where the ζ is zero (Fig. 2 and 3; Table 1). Variations in the IEP values are due to the heterogeneities within the chemical compositions and clay mineralogy (since clays are the most reactive in determining the charge characteristics such as IEP of shales) (Fig. 1 and Table 1) [36]. Q1, Q2, Q3 and Q4 reported relatively low IEP values of 2.40, 2.61, 3.08 and 3.62 respectively. The dominance of kaolinite clay mineral in the samples may account for such low values [14]. Authors such as [14][37][38] reported similar values within the pH range of 2-4 for kaolinitic rich samples.

The isoelectric point determined from electrophoretic mobility is quite intriguing for Q5. At first glance, one would expect the sample to report an IEP of about 6 which is an average of the IEPs of kaolinite (average IEP ~ 3) and goethite (~ 9) since these are the two main minerals the sample is composed of. However, the particles of Q5 shifted more toward the anode under the influence of an electric field thereby registering an IEP of 7.92 which is closer to that of goethite (Fig. 3). This implies that the kaolinites in Q5 do not contribute to its surface charge properties. The high percentages of Fe_2O_3 and the presence of goethite in the

sample could possibly have shifted the IEP towards the IEP values of oxidic minerals such as goethite reported [1].

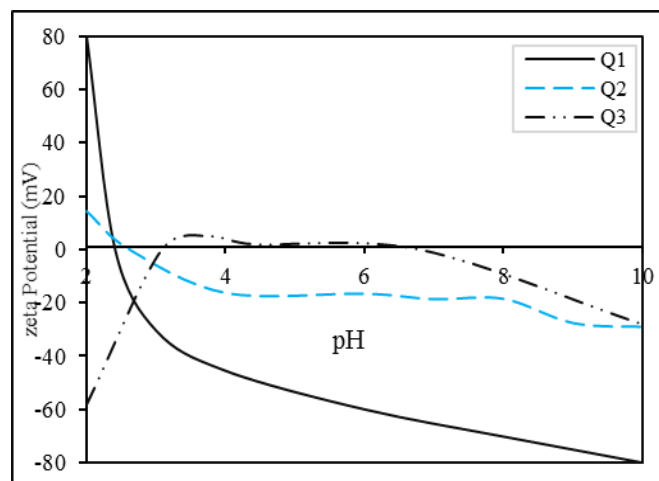


Figure 2: Zeta Potential of Q1, Q2 and Q3 as a Function of pH

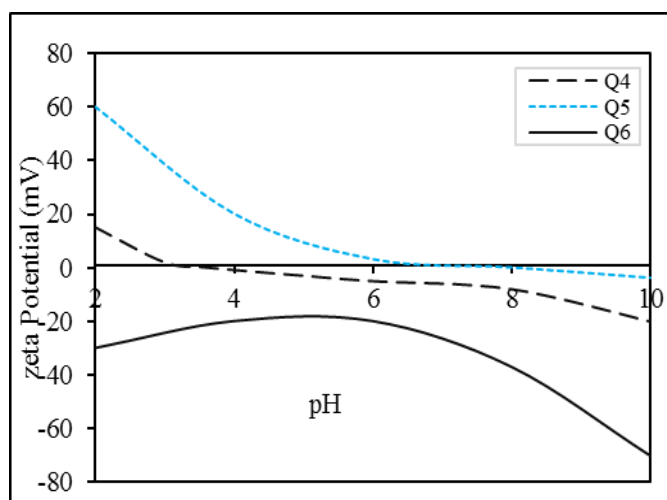


Figure 3: Zeta Potential of Q4, Q5 and Q6 as a Function of pH

Relationship Between IEP and Fe_2O_3

Although the main objective is to investigate the surface charge properties and document the associated IEP of the Setap Formation of the Sarawak basin using a faster approach, an attempt has been made to relate the Fe_2O_3 concentration to the pH(s) at which the samples were least stable (IEP) (Table 1) under an electric field. Fig 4 is a representation of the correlation between IEP and the Fe_2O_3 concentrations of the five samples that reported IEP.

The relationship between Fe_2O_3 and IEP was positive as expected with correlation (r^2) of 0.62 (Fig 4). This relationship is consistent with those obtained by [37]. The positive correlation supports the earlier suggestion that the presence of oxidic minerals such as goethite ($\text{FeO}(\text{OH})$) is the cause of the shift or relatively high IEP reported in Q5.

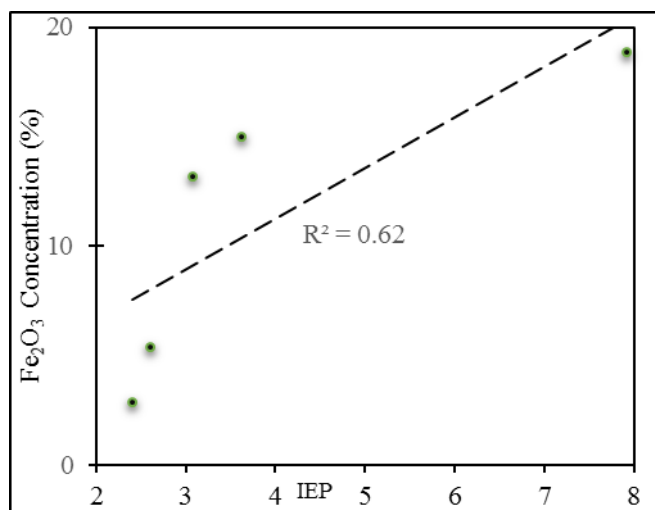


Figure 4: Relation between IEP and Sample Oxide Content

Conclusions

The study of the surface potential behaviour of six shale samples from the Setap Formation in Malaysia using electrophoretic mobility showed that the ζ of particles ranged from -80 mV to + 80 mV. All samples but one reported IEP. The variable IEP values (2.4-7.92) reported for Q1-Q5 indicate that there is a variability in the ion receptive capacities (sorption capacity) in the Setap Formation. The relatively high IEP (7.92) of Q5 due to the shift by the oxidic mineral goethite and the confirmation by the positive correlation between Fe₂O₃ and IEP indicates that Fe₂O₃ also has a strong influence on the sorption capacities of the shales. The absence of IEP in Q6 is due to the failure of the variable charges to compensate the high in magnitude structural charges on the sample. Such negligible influence of the pH dependent charges also account for the electronegative behaviour of the sample throughout the range of pH of the study.

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