

Spectral induced polarization (SIP) response of biodegraded oil in porous media

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SUMMARY

Laboratory experiments were conducted to investigate the effect of different oil saturation (0.2–0.8), wetting conditions (water-wet and oil-wet), and the addition of asphaltene on the spectral induced polarization (SIP) response of biodegraded and fresh crude oil in sand columns. In the water-wet case, no significant differences were observed for both the fresh and biodegraded oil and both displayed an increase in the magnitude of the phase (φ) and decrease in the magnitudes of the real (σ') and imaginary (σ'') conductivity components with increasing oil saturation. In this instance the SIP response is most likely controlled by the conduction and polarization of the electric double layer at the mineral–water interface. However, when oil is the wetting phase there were considerable differences in the magnitude of the SIP parameters between the fresh and biodegraded oil. The magnitude of φ and σ'' increased with increasing oil saturation, whereas σ' decreased. The magnitude of σ' and σ'' for the biodegraded oil-wetted sands were relatively higher compared to fresh oil-wetted sands. In experiments with fresh and biodegraded oil-wet sand, the addition of 1 per cent asphaltene increased σ' and σ'' with the biodegraded oil showing the highest magnitude. Asphaltenes are the most dipolar fraction of crude oil and increase in concentration with increasing biodegradation. Asphaltene creates a surface charge due to the ionization and complexation reactions of functional groups at interfaces. Therefore, the enhancement in the conduction and polarization observed with the biodegraded oil-wetted sands may be due to the increase in polar components (e.g. asphaltene) from the biodegradation process and the interactions of the polar components with the surfaces of water and mineral grains. Further studies are required to investigate the effect of other components in biodegraded oil such as resins, trace metals, biogenic metallic minerals (e.g. magnetite) and organic acids on the SIP response of porous media.

Key words: Electrical properties; Hydrogeophysics; Hydrology; Permeability and porosity.

1 INTRODUCTION

Oil spills continue to represent a widespread environmental problem, threatening water supplies and contaminating coastal environments. Over the past three decades, a variety of geophysical techniques have been applied at hydrocarbon contaminated sites to detect the presence of the hydrocarbons, as well as assess the presence of intrinsic bioremediation (for an extensive review see Atekwana & Atekwana 2010). Among the different geophysical techniques, spectral induced polarization (SIP) has emerged as a promising and sensitive technique to determine the presence of hydrocarbon contaminants (Olhoeft 1985; Börner *et al.* 1993; Schmutz *et al.* 2010, 2012; Revil *et al.* 2011; Flores Orozco *et al.* 2012; Schwartz *et al.* 2012) as well as the accompanying biophysicochemical changes associated with hydrocarbon biodegradation (Abdel Aal *et al.* 2004, 2006; Mewafy *et al.* 2013).

The wettability, saturation and physicochemical properties of the organic contaminant are among the important factors that strongly

affect the SIP signatures of oil bearing sediments (Schmutz *et al.* 2010, 2012; Revil *et al.* 2011). Wettability is defined as the tendency of a fluid to adhere or adsorb to a solid surface in the presence of another immiscible fluid (Anderson 1986). In an oil-contaminated site, it is a measure of the affinity of the soil mineral surface for the oil or water phase (Craig 1971). Wettability strongly affects the distribution of saturation fluids (e.g. water and oil) in the pore space, the connectivity of the conducting phase (water) and charge transport in the medium (Capaccioli *et al.* 2000). Therefore, the SIP response of the oil contaminated sediments may vary according to the wetting phase, the relative saturation, the geometric distribution of the wetting and non-wetting fluids and the chemical composition of the oil (Schmutz *et al.* 2010, 2012; Revil *et al.* 2011).

Different laboratory and field SIP signatures are reported for organic contaminants in porous media. Laboratory measurements on samples containing clay minerals contaminated with petroleum hydrocarbons show an increase in the phase values (φ) for SIP at low frequencies (<10 Hz) due to the enhancement in surface

polarization from adsorption of organic cations onto the clay surfaces (Olhoeft 1985; Vanhala *et al.* 1992). Börner *et al.* (1993) observed an increase in the magnitude of the phase in clays in the presence of non-wetting organic contaminants and a decrease in the magnitude of the phase for oil-contaminated sandstones except for the case of benzene. Vanhala (1997) showed that the introduction of fresh oil decreases the magnitude of the phase of glacial sediments (sands and tills), although changes were observed with continued oil maturation time. More recently, Ustra *et al.* (2012) conducted laboratory SIP measurements for 40 d on clayey soils contaminated with varying amount of toluene. The results show that the SIP response is highly dependent on the toluene content at the early stage of the experiment and that the changes become more dependent on the clay content towards the end of experiment as samples reach equilibrium in electrical response. Ustra *et al.* (2012) argue that the poor correlation between toluene and the obtained parameters of the Debye decomposition indicate that this procedure, which likely integrates multiple mechanisms, may not be suitable for understanding relationships between SIP and hydrocarbon contamination. Recent studies have reported an increase in the time constant (τ) values for SIP measurements collected in samples with different saturation of non-aqueous phase liquids (e.g. octanol) (Cassiani *et al.* 2009). The authors concluded that changes in SIP responses are caused by pore obstruction by electrically non-conductive liquids and not by the electrochemical effects at the grain–electrolyte interface. Schmutz *et al.* (2010) extended the model proposed by Revil & Florsch (2010) to fit laboratory data collected in sand samples with different grain sizes contaminated with non-wetting fresh oil. Schmutz *et al.* (2010) modelled a decrease in the imaginary part of the complex conductivity (σ'') with increasing oil (i.e. non-aqueous phase) saturation. However, when oil was the wetting phase, the magnitude of the phase and resistivity decreased with increasing oil saturation which Schmutz *et al.* (2010) interpreted as resulting from the increase in the cation exchange possibly associated with the presence of a polar component at the oil–water interface (Revil *et al.* 2011). More recently, Schmutz *et al.* (2012) investigated the effect of saturation of different oil types on the complex conductivity signatures of non-wet oil sand and observed that for the same sample, the quadrature conductivity first increased with saturation and then decreased, indicating that two processes compete in controlling the quadrature conductivity. They also concluded that the quadrature conductivity appears to be influenced not only by the value of the saturation exponent, but also by the surface area between the oil phase and the water phase. At the field scale, complex conductivity measurements have been used to characterize the extent of contamination in an aquifer underlying a landfill (Aristodemou & Thomas-Betts 2000; Dahlin *et al.* 2002) and to delineate the presence of petroleum hydrocarbon due to fuel spills using single frequency data collected with electrodes placed in boreholes (Kemna *et al.* 2004a) and surface time-domain measurements (Sogade *et al.* 2006; Flores Orozco *et al.* 2012).

To date the effect of oil-wettability and saturation on SIP response provides experimental data for mostly fresh oil (Schmutz *et al.* 2010, 2012; Revil *et al.* 2011). However, these results differ significantly from laboratory and field investigations where the oil is mostly in the biodegraded state (Abdel Aal *et al.* 2004, 2006; Mewafy *et al.* 2013). The activity of microorganisms naturally found in the subsurface might lead to the attenuation of contaminants or their transformation into less toxic compounds through metabolic or enzymatic processes (Cozzarelli *et al.* 1994, 2001; Cassidy *et al.* 2002). It is well known that microbial biodegradation significantly affects the physical properties and molecular composition of crude oil, lead-

ing to a decrease in low molecular weight organic compounds and an increase in the polar fraction, viscosity, density, sulphur content and acidity (Connan 1984; Peters *et al.* 2005; Larter *et al.* 2006). Petroleum biodegrading organisms have a specific order of preference for compounds that they remove from oils. The early stages of oil biodegradation are characterized by the loss of *n*-paraffins and acyclic isoprenoids (Larter *et al.* 2006). Progressive degradation of crude oil tends to concentrate heavy polar and asphaltene components in the residual hydrocarbon which have the greatest impact on oil density, viscosity and wetting conditions (Larter *et al.* 2006). The increase in polar components (e.g. asphaltenes) with their surface-active properties, have the potential to alter the surface wettability of crude oil impacted sediments from the interaction of their polar functional groups with the surface polar sites (Miiller *et al.* 1987; Sayyoub *et al.* 1991; Standal *et al.* 1999). The induced biophysico-chemical changes in the crude oil properties due to biodegradation have the potential to impact the SIP signature of oil-contaminated sediments. SIP measurements on samples retrieved from hydrocarbon contaminated sites undergoing biodegradation have suggested higher magnitude of imaginary conductivity and phase compared to samples from uncontaminated locations (Abdel Aal *et al.* 2006; Mewafy *et al.* 2013). In the study by Abdel Aal *et al.* (2006) study, the authors concluded that the enhanced SIP response might occur due to pore constrictions as a consequence of ion-selective biological membranes, while the study by Mewafy *et al.* (2013) study suggested an enhancement in the polarization due to the presence of biometallic mineral phases resulting from microbial mediated redox processes. The SIP response at hydrocarbon contaminated sites undergoing biodegradation is not fully understood and the contribution of the biodegraded oil under different wettability and saturation conditions has not been documented. For instance, during microbial degradation of hydrocarbon, bacteria produce metabolic intermediates such as biosurfactants (surface active agents; Cassidy *et al.* 2002). The biosurfactants produced by microorganisms enhance the solubility and reduce the surface tension of the hydrocarbon fraction adsorbed on the mineral grain surfaces causing wettability alteration (Karimi *et al.* 2012). Therefore the SIP response at hydrocarbon contaminated site undergoing biodegradation may result from changes in wettability.

In this study, we extend the work of Schmutz *et al.* (2010) and Revil *et al.* (2011) by investigating the SIP response of biodegraded oil in porous media under different saturation and wettability conditions. We conducted laboratory experiments to investigate the effect of different oil saturation (0.2–0.8), wetting conditions (water-wet and oil-wet), and evaluated the role of asphaltenes on the SIP response of biodegraded and fresh oil in sand columns. Our results provide important insights into the contribution of biodegraded oil to the SIP response of hydrocarbon contaminated sediments undergoing biodegradation and under different saturation and wettability conditions as well as shallow oil reservoirs where crude oil is subject to different levels of biodegradation.

2 THEORETICAL BACKGROUND

The SIP method (also called complex resistivity or complex conductivity) is an extension of the electrical resistivity method. In SIP we consider both the magnitude and phase lag between voltage and current in a broad frequency range typically from 1 mHz to few tens of kHz (<100 Hz in the field). SIP parameters are determined from measurements of the resistivity (or conductivity) magnitude $|\rho|$ (or $|\sigma|$) and the phase shift φ between a

measured voltage sinusoid using two voltage electrodes M and N and an impressed current sinusoid using two current electrodes A and B. Stating in terms of complex conductivity;

$$\sigma^* = (1/\rho^*), \quad \sigma^* = \sigma' + i\sigma'', \quad (1)$$

where the real and imaginary conductivities, σ' and σ'' , are frequency dependent and defined from the measured parameters ($|\sigma|$ and ϕ),

$$\begin{aligned} \sigma' &= |\sigma| \cos \phi \\ \sigma'' &= |\sigma| \sin \phi. \end{aligned} \quad (2)$$

The in-phase (real, σ') conductivity component represents ohmic conduction currents (energy loss) that contain an electrolytic (σ_{el}) and interfacial (σ'_{surf}) component (Lesmes & Frye 2001). The σ'_{surf} results from surface conduction via the formation of an electrical double layer (EDL) at the grain–fluid interface (Revil & Glover 1998). A common assumption is that the electrolytic conductivity (σ_{el}) and surface conductivity (σ'_{surf}) add in parallel (Vinegar & Waxman 1984):

$$\sigma'(\sigma_w) = \sigma_{el} + \sigma'_{surf} = \left(\frac{1}{F}\right) + \sigma'_{surf}, \quad (3)$$

where σ' is a function of fluid chemistry σ_w and F is the formation factor. The out of phase (imaginary, σ'') conductivity represents the much smaller polarization (energy storage) term which at low frequencies (<1000 Hz) is modelled as a function of the physico-chemical properties of the grain–fluid interface (Vinegar & Waxman 1984; Börner *et al.* 1996; Lesmes & Frye 2001; Slater & Lesmes 2002). Conduction and polarization at this interface is a function of surface area, surface charge density, surface ionic mobility and surface tortuosity (Schön 1996; Revil & Glover 1998; Lesmes & Frye 2001).

Laboratory studies using unsaturated unconsolidated sediments show that polarization and conduction at low frequencies (<1000 Hz) exhibit power-law dependency on saturation with a smaller exponent for σ' (polarization) magnitude compared to σ' (conduction) magnitude (Ulrich & Slater 2004). Schmutz *et al.* (2010) extended the model proposed by Revil & Florsch (2010) to fit laboratory data collected in water-wet sand samples partially saturated with oil using the following power-law relationships:

$$\sigma' = \sigma_f \phi^m S_w^n \quad (4)$$

$$\sigma'' = c S_w^p \quad (5)$$

$$\phi_m = a S_w^{-b}, \quad (6)$$

where σ_f is the pore water conductivity, ϕ is the porosity, m is the cementation factor, S_w is the water saturation, n is the saturation exponent for the inphase (real) conductivity, p is the saturation exponent for the quadrature (imaginary) conductivity, c ($S m^{-1}$) and a (mrad) are proportionality coefficients defined in Schmutz *et al.* (2010) (eqs 36 and 34, respectively), ϕ_m is the phase at low frequency relaxation and b is an exponential coefficient (mrad). Eq. (4), the second Archie's law, is valid only in the absence of surface conductivity and $n > 1$. Eq. (5) has been proposed by Vinegar and Waxman (1984) with $p = n - 1$. However, the Schmutz *et al.* (2012) study on sand partially saturated with different types of non-wetting oils showed that the relationship $p = n - 1$ is not always valid which according to the authors may be related to the fractal nature of the oil–water interface.

Previous studies have also documented that the polarization response may change at the pore throats filled with fluid due to localized ionic constriction in the pore space, and a correlation between pore throat size and relaxation time has been established (Scott & Barker 2003, 2005; Binley *et al.* 2005). A small narrow pores (SNP) model was proposed by Titov *et al.* (2002) and represents a special case of the original membrane polarization model of Marshall & Madden (1959). More recently, Scott (2006) suggests that the pore throat is the controlling factor in relaxation even when polarization is dominated by EDL ion diffusion (possibly in the Stern layer).

3 MATERIALS AND METHODS

Three different laboratory experiments were conducted to investigate the effect of (i) oil saturation, (ii) wetting conditions (water-wet and oil-wet) and (iii) the presence of asphaltene on the SIP response of fresh and biodegraded oil in sand columns. Fresh oil (non-degraded) is used here to compare the results with biodegraded oil. The following is a brief description of the materials and experimental procedures for each experiment.

3.1 Column construction and SIP setup

The setup of the SIP measurements comprises a sample holder/columns constructed from polyvinyl chloride (PVC) pipe with an inner diameter of 3.17 cm and a length of 12 cm (Fig. 1). Four non-polarizing Ag–AgCl electrodes housed in electrolyte (agar gel mixed in 3 M concentration of KCl) filled chambers were placed 2 cm apart along the length of the column and located just outside the current flow path. The outer two electrodes were used to inject the current sinusoid and the two inner electrodes were used to record the output voltage sinusoid. Two rubber stoppers were used to cap the two ends of the column after packing with sand–fluids mixture. The four non-polarizable electrodes were connected to a dynamic signal analyser (DSA) NI-4461 to perform the SIP measurements between 0.1 and 1000 Hz at 13 equal logarithmic intervals (with a sensitivity of 0.1 mrad below 100 Hz frequency range determined by measuring the phase response of artificial ground water (AGW) with known conductivity and comparing it to the theoretical response assuming a relative dielectric permittivity of 81). An AD620 preamplifier boosted the input impedance on the voltage channel and prevented current leakage into the circuitry. The impedance magnitude $|\sigma|$ and the phase shift ϕ (between a measured voltage sinusoid and an impressed current sinusoid) of the sample were measured relative to a high-quality resistor (Slater & Lesmes 2002). The real ($\sigma' = |\sigma| \cos \phi$) and imaginary ($\sigma'' = |\sigma| \sin \phi$) parts of the sample complex conductivity were then calculated.

3.2 Porous media, fluids and asphaltene preparation

The porous medium used to fill the columns consisted of fine silica Ottawa sands (U.S. Silica Company) with a median grain diameter distribution $d_{50} = 200 \pm 10 \mu m$ and a porosity of 0.45 ± 0.02 (calculated from the total volume of the column minus the volume of the dry sand). The formation factor of the sand at full saturation with the water phase was 3.19 and obtained from the measured σ' as a function of σ_w (0.02 – $0.12 S m^{-1}$ for AGW).

The fluids used for the saturation and wettability experiments were AGW, fresh and biodegraded oils. The AGW is similar to that used by Abdel Aal *et al.* (2009) with electrical conductivity of $0.98 \pm 0.3 \times 10^{-2} S m^{-1}$ and pH (7.01 ± 0.01). The fresh oil

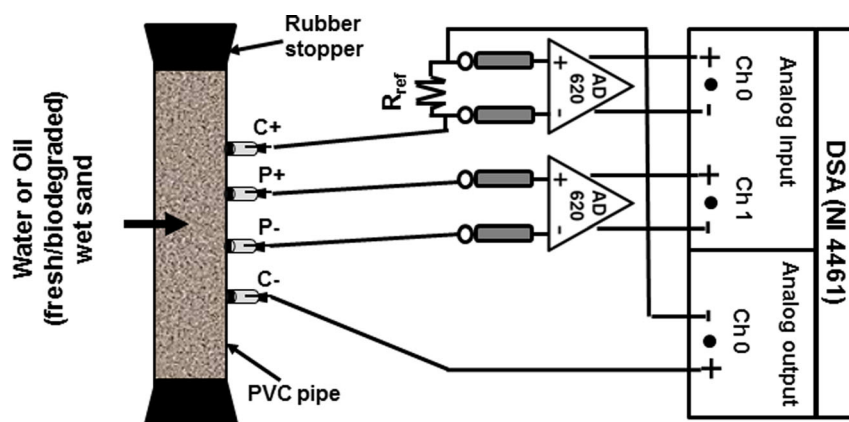


Figure 1. Schematic of column setup (left-hand side) and instrumentation used in SIP measurements (right-hand side).

sample was supplied by Enbridge Energy (Ltd.), whereas the biodegraded oil sample was collected from the National Crude Oil Spill Fate and Natural Attenuation Research Site at Bemidji, MN. The site is undergoing active biodegradation for almost 30 yr and has been the focus of intensive geochemical (Cozzarelli *et al.* 2010) and microbiological studies (Bekins *et al.* 2001). The site is characterized by a biogeochemical process where iron reduction is coupled with the oxidation of hydrocarbon contaminants. The biodegraded oil sample was collected from the free phase contaminated location where microbial induced magnetite precipitation is known to occur in the bulk sediment (Tuccillo *et al.* 1999; Mewafy *et al.* 2011).

The effect of asphaltene was studied here because it is one of the main components of crude oil having unique properties that can potentially impact the electrical properties of oil-impacted sediments. Asphaltenes comprise a major portion of surface active crude oil components (Sjoblom *et al.* 2003) and are defined as the crude oil fraction insoluble in alkanes such as pentane or heptane and soluble in toluene. Asphaltenes are typically present in crude oil in the range of 0–10 per cent or more and have a dramatic effect on chemical and physical properties of the crude oil (Joshi *et al.* 2001). Asphaltenes are polyaromatic compounds of large molecular weight, ranging from less than 500 to 2000 g mol⁻¹ (Hortal *et al.* 2006). Asphaltenes are flat sheets and the molecules are composed of condensed (fused) aromatic rings linked with aliphatic chains and naphthenic rings (Altamirano *et al.* 1986). They include a large variety of chemical species, containing sulphur, nitrogen, oxygen, heavy metals (vanadium, nickel and iron) and functional groups such as acids and bases (Strausz *et al.* 1992; Peng *et al.* 1997). Asphaltenes can also adsorb onto different surfaces, being responsible for particle wettability alteration (Buckley & Liu 1998). They have a strong tendency to self-associate and form aggregates (Goncalves *et al.* 2004).

Asphaltenes can be separated from crude oil by several procedures and the results will vary according to the method used. Here, we used the ASTM recommended procedure for separating asphaltenes from crude oil (ASTM D2007–80) which is a widely accepted standard procedure. The asphaltenes were precipitated by dissolving 2 g of asphalt (obtained from a refinery site) in 25 ml toluene with continuous stirring and then mixed with *n*-hexane (1:40 v/v) for 24 hr at room temperature. The mixture was centrifuged at 2400 rpm for 10 min to separate the heaviest fraction (asphaltenes) and the whole process was repeated several times until the desired amount of asphaltene was obtained. The separated fraction of asphaltenes was dried at room temperature, crushed to fine particles (~15 µm) and was ready for use. To determine the asphaltene con-

tent of both the fresh and biodegraded oil samples, 1 ml of crude oil was mixed with 40 ml of *n*-hexane and left at room temperature for 24 hr. The mixture was then centrifuged at 2400 rpm for 10 min and the supernatant was decanted and the separated asphaltenes was air dried and weighed. The asphaltene content as dry weight was determined to be 9 and 16 per cent for fresh and biodegraded oil, respectively.

3.3 Experimental procedure

All experiments were conducted at ambient laboratory temperature, typically 22 ± 1 °C. Two different wettability conditions [water-wet (Fig. 2a) and oil-wet (Fig. 2b)] were investigated using a mix of sand, AGW and oil (fresh and biodegraded) samples following the procedure of Schmutz *et al.* (2010) and Revil *et al.* (2011) where the experimental wettability conditions were simply defined according to the order of AGW versus oil mixed with sand. The amount of sand is fixed and the required pore volume to completely saturate the sand has been determined from the difference in weight of dry and fully saturated sand. Based on the determined pore volume, the volumes of oil and water were calculated to obtain the desired oil and water saturations with a final total saturation (AGW + oil) of 100 per cent. To avoid the error in fluid volume, a peristaltic pump was used to precisely deliver the exact desired volume of AGW and oil samples to be mixed with the fixed amount of sands. Furthermore, the total preparation time of mixing of fluids with sands and SIP measurements were made short and constant (10 min) for all experimental treatments. The purpose was to minimize the effect of any possible chemical reaction that may occur over time and change the measured SIP signature, if the samples are prepared and measured at different times. The experiments for water-wet and oil-wet cases were conducted at five different water saturations ($S_w = 1, 0.8, 0.6, 0.4$ and 0.2), which correspond to five different oil saturations ($S_o = 0, 0.2, 0.4, 0.6$, and 0.8). The measurements at 100 per cent oil saturation ($S_o = 1$) could not be achieved because of the high contact resistance associated with the high resistivity of the oil.

In the case of water-wet sand partially saturated with fresh or biodegraded oil samples, the AGW is the wetting fluid forming a continuous film coating the sand grain surfaces whereas the oil is the non-wetting fluid filling the small pore space (Fig. 2a-i). In this case the AGW was added first and mixed very well with the sand (Fig. 2a-ii) and then fresh or biodegraded oil was added and mixed very well (Fig. 2a-iii). The water-oil-sand mixture was packed onto the constructed sample holder (PVC column; Fig. 2-iv) and SIP

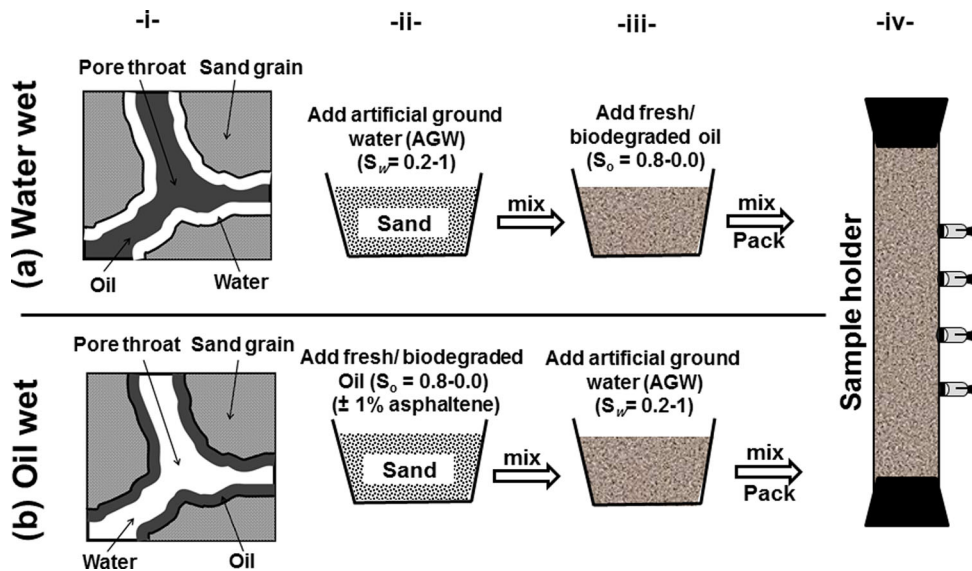


Figure 2. Schematic representation of the experimental procedure (a) water-wet case and (b) oil-wet case.

measurements were obtained in the frequency range from 0.1 to 1000 Hz. The same procedure was repeated for the oil-wet case except that the oil samples (fresh or biodegraded) were first added to the sands followed by the addition of the AGW (Figs 2b-i-iv). In the oil-wet case, the oil is the wetting fluid coating the sand grain surfaces with the AGW filling the pore space (Fig. 2b-i). The schematic representations of the distribution of the wetting and non-wetting fluids shown in Fig. 2 are considered to be a simplification of the real picture of the field impacted oil sediments.

The effect of packing on the SIP measurements was investigated for several samples during the course of the experiments. Here, we show an example of the SIP measurements acquired for two separate and identically prepared oil-wet sands samples A and B ($S_w = 0.2$) partially saturated with 80 per cent biodegraded oil. The phase response of the two identical oil-wet samples (A and B with average values (solid line) and error bars) show that the effect of packing on the magnitude of phase response was small (± 1 mrad; Fig. 3).

The asphaltene experiment was conducted for oil-wet samples with 50 per cent oil saturation and 50 per cent AGW saturation ($S_o = 0.5$ and $S_w = 0.5$). About 1 per cent dry weight (w/w of oil)

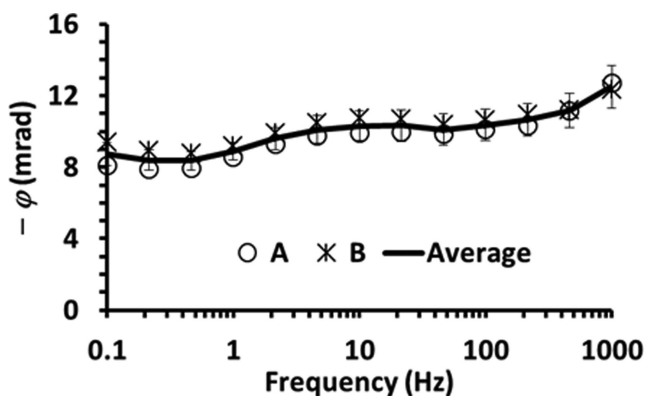


Figure 3. The measured phase response (φ) of two separate and identical biodegraded oil-wet samples (A and B) with average values (solid line) and error bars. The percentage change in the magnitude of φ for the two measured samples is less than 1 per cent.

of the crushed asphaltene was mixed first with fresh or biodegraded oil sample and then the mixture was added to the sand followed by AGW as described above. The SIP measurements were collected in the frequency range 0.1–1000 Hz for fresh and biodegraded oil-wet sands with and without asphaltene.

4 RESULTS

The SIP results are presented as ‘water-wet case’, ‘oil-wet case’ and ‘effect of asphaltene’.

4.1 Water-wet case

For the case of water-wet sand partially saturated with fresh oil, the absolute value of the phase (φ) increases with increasing oil saturation with a relaxation peak below 100 Hz (Fig. 4a). The relaxation peak of the phase is more defined at 10 Hz frequency and at higher oil saturation (Fig. 4a). At 10 Hz, φ increases from 1.09 mrad at $S_w = 1$ to 7.29 mrad at $S_w = 0.2$. On the other hand, both the magnitude of the imaginary (σ'') and real (σ') conductivity decreases with increasing oil saturation as shown in Figs 4(b) and (c), respectively. At 10 Hz, σ'' decreases from $3.44 \times 10^{-6} \text{ S m}^{-1}$ at $S_w = 1$ to $2.46 \times 10^{-6} \text{ S m}^{-1}$ at $S_w = 0.2$, whereas σ' decreases from $31.32 \times 10^{-4} \text{ S m}^{-1}$ at $S_w = 1$ to $3.38 \times 10^{-4} \text{ S m}^{-1}$ at $S_w = 0.2$. Within the oil saturation range used in this experiment (0.0–0.8), φ and σ' change within one order of magnitude (Figs 4a and c, respectively) compared to less than a quarter order of magnitude for σ'' (Fig. 4b). These results are consistent with results presented by Schmutz *et al.* (2010) and Revil *et al.* (2011) for non-wetting oil.

Similar observations were obtained in the case of water-wet sand partially saturated with biodegraded oil (Fig. 5). At 10 Hz, φ increases from 1.09 mrad at $S_w = 1$ to 5.56 mrad at $S_w = 0.2$ (Fig. 5a). Whereas σ'' decreases from $3.44 \times 10^{-6} \text{ S m}^{-1}$ at $S_w = 1$ to $2.40 \times 10^{-6} \text{ S m}^{-1}$ at $S_w = 0.2$ (Fig. 5b), and σ' decreases from $31.32 \times 10^{-4} \text{ S m}^{-1}$ at $S_w = 1$ to $4.32 \times 10^{-4} \text{ S m}^{-1}$ at $S_w = 0.2$ (Fig. 5c).

The power-law trend lines (using eqs 3–5) for the SIP data (φ , σ'' and σ') at 10 Hz as a function of water saturation for both water-wet sand partially saturated with fresh (opened circles) and biodegraded

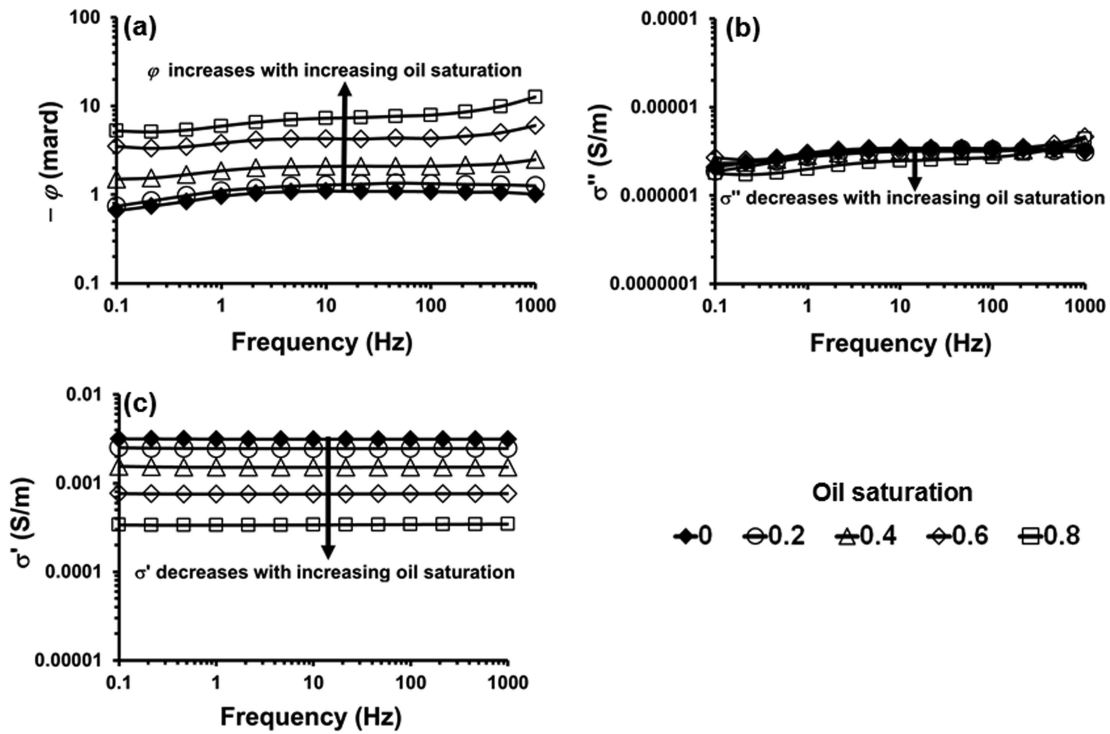


Figure 4. SIP results (a) phase (φ), (b) imaginary conductivity (σ'') and (c) real conductivity (σ') of water-wet sand partially saturated with fresh oil. Absolute values of φ increased with increasing oil saturation whereas both σ'' and σ' decreased. Both φ and σ'' spectra show well-defined relaxation peaks at frequencies below 100 Hz.

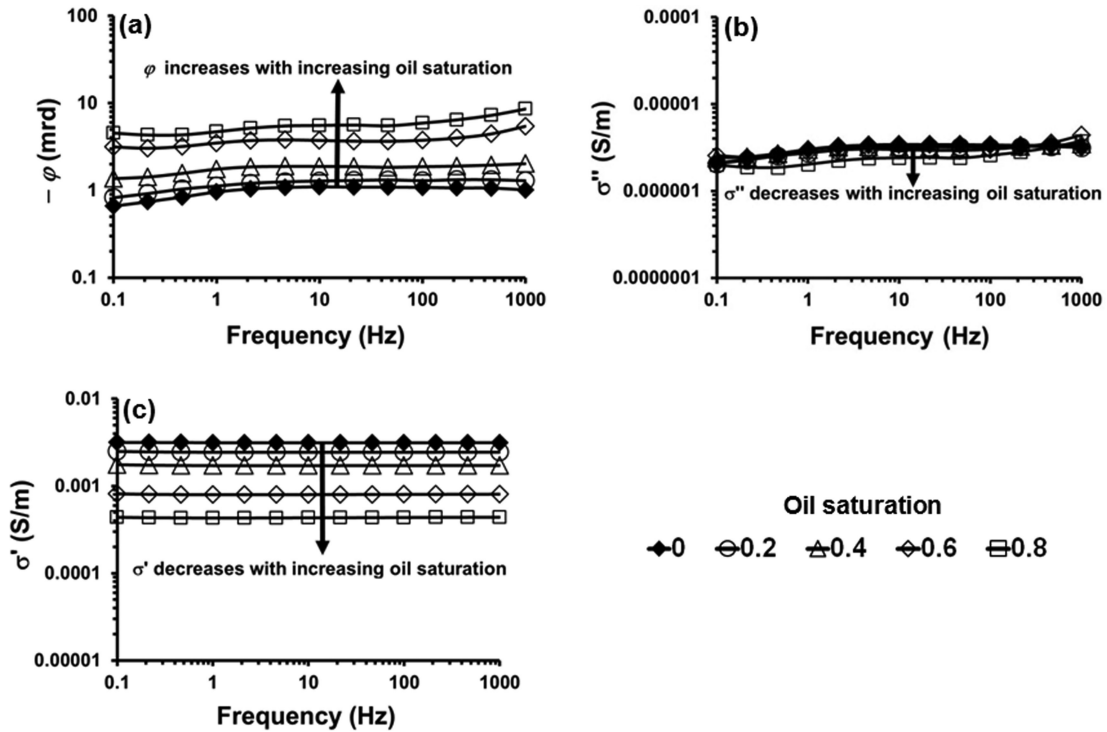


Figure 5. SIP results (a) phase (φ), (b) imaginary conductivity (σ'') and (c) real conductivity (σ') of water-wet sand partially saturated with biodegraded oil. Absolute values of φ increased with increasing oil saturation whereas both σ'' and σ' decreased. Both φ and σ'' spectra show well-defined relaxation peaks at frequencies below 100 Hz.

(filled circles) oil samples show no differences in the rate of change of SIP parameters as a function of water–oil saturation (Fig. 6). However, at higher oil saturation ($S_o > 0.6$ or $S_w < 0.4$), the trend lines show slightly higher φ and lower σ' for fresh oil compared to

biodegraded oil (Figs 6a and c, respectively). The good of fitness (R^2) for the φ and σ' power-law trend lines is higher (~ 0.9) than the σ'' (~ 0.7). The saturation exponent (n) of the fresh oil ($n = 1.432$) is relatively higher than the biodegraded oil ($n = 1.283$) as shown

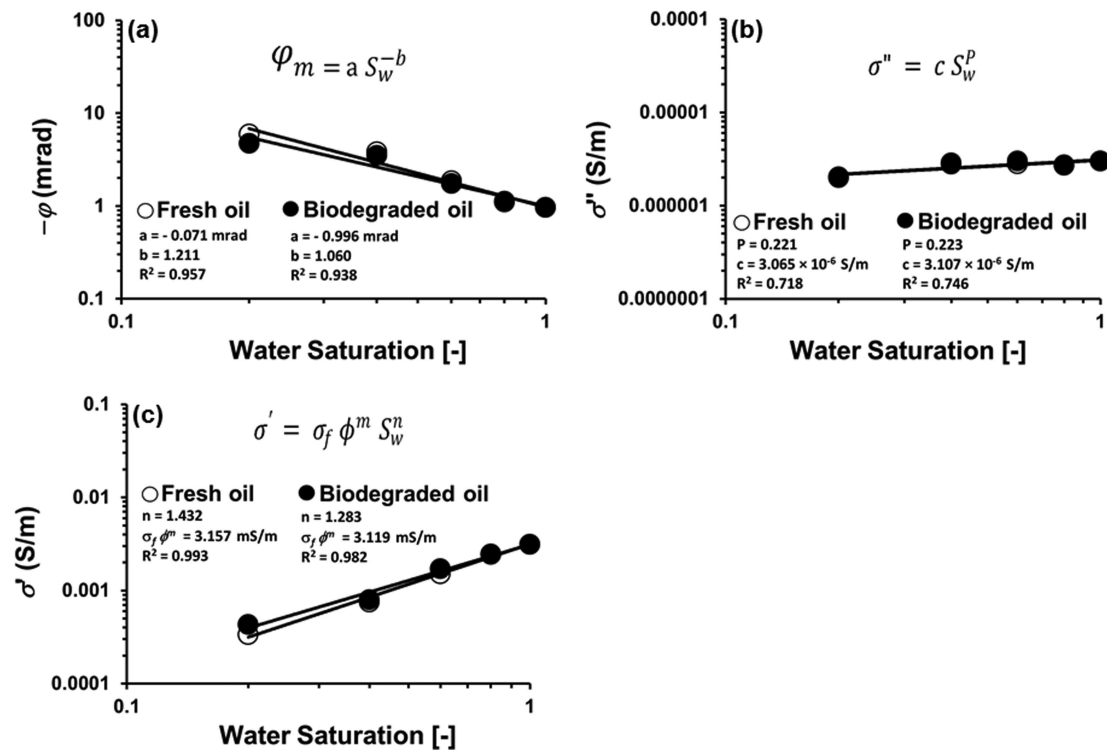


Figure 6. SIP results at 10 Hz (a) phase (φ), (b) imaginary conductivity (σ'') and (c) real conductivity (σ') of water-wet sand partially saturated with fresh oil (open circles) and biodegraded oil (filled circles) fitted with the power-law trend line using eqs (4)–(6). Minimal difference is observed in the SIP response of fresh and biodegraded oil.

in Fig. 6(c). However, the saturation exponents (p) of the fresh oil ($p = 0.221$) and biodegraded oil ($p = 0.223$) are nearly the same (Fig. 6b). The saturation exponents (p) for the σ'' do not follow the relationship $p = n - 1$ as proposed by Vinegar and Waxman (1984) which is similar to the observations by Schmutz *et al.* (2012) for non-wetting and strongly water-repellent oils.

4.2 Oil-wet case

For the oil-wet sand partially saturated with fresh oil, the absolute value of φ increases with increasing oil saturation with a relaxation peak below 100 Hz (Fig. 7a). The relaxation peak of φ is also more defined at 10 Hz frequency and higher water saturation (Fig. 7a). At 10 Hz, φ increases from 1.09 mrad at $S_w = 1$ –15.84 mrad at $S_w = 0.2$ (Fig. 7a). On the other hand, both the magnitude of σ'' and σ' conductivity decreases with increasing oil saturation (Figs 7b and c, respectively). At 10 Hz, σ'' decreases from 3.44×10^{-6} S m⁻¹ at $S_w = 1$ to 1.83×10^{-6} S m⁻¹ at $S_w = 0.2$ (Fig. 7b), whereas σ' decreases from 31.32×10^{-4} S m⁻¹ at $S_w = 1$ to 1.16×10^{-4} S m⁻¹ at $S_w = 0.2$ (Fig. 7c). φ and σ' change within one order of magnitude (Figs 7a and c, respectively) compared to less than a quarter order of change in σ'' magnitude (Fig. 7b) within the oil saturation range used in this experiment (0.0–0.8).

For the case of oil-wet sand partially saturated with biodegraded oil, the absolute value of the phase (φ) and σ'' increases with increasing oil saturation (Figs 8a and b, respectively), whereas σ' decreases (Fig. 8c). At 10 Hz, φ increases from 1.09 mrad at $S_w = 1$ to 9.90 mrad at $S_w = 0.2$ (Fig. 8a), whereas σ'' increases from 3.44×10^{-6} S m⁻¹ at $S_w = 1$ to 4.52×10^{-6} S m⁻¹ at $S_w = 0.2$ (Fig. 8b). However, at 10 Hz, σ' decreases from 31.32×10^{-4} S m⁻¹ at $S_w = 1$ to 4.05×10^{-4} S m⁻¹ at $S_w = 0.2$ (Fig. 8c).

The SIP data at 10 Hz of the oil-wet sand partially saturated with fresh oil and biodegraded oil was not fitted with the power-law equations because there is no theory developed yet for oil as the wetting phase. However, a trend line was used as a guide to the eyes to examine the relationships (Fig. 9). The oil-wet sand partially saturated with fresh (open circles) and biodegraded (filled circles) oil samples show a difference in the rate of change of SIP parameters at 10 Hz as a function of water–oil saturation especially at higher oil saturation ($S_o > 0.6$ or $S_w < 0.4$). The solid lines show that φ for fresh oil-wet samples was slightly higher in magnitude than biodegraded oil-wet samples, with both showing a decrease in the absolute values of φ with increasing water saturation (Fig. 9a). In addition, the biodegraded oil-wet sands show higher σ'' and σ' magnitudes compared to fresh oil-wet sands at S_w equal to or less than 0.6 (Figs 9b and c, respectively). Moreover, the trend lines show that σ'' and σ' generally increase with increasing water saturation (Figs 9b and c, respectively) except for σ'' of the biodegraded oil, which to some extent, decreases with increasing water saturation up to 60 per cent which increases thereafter (Fig. 9b).

4.3 Effect of asphaltene

The real (σ') and imaginary (σ'') conductivity results of the 50 per cent oil-wet samples without asphaltene (open symbols) show lower magnitude for the fresh oil (circles) compared to biodegraded oil (diamonds; Fig. 10) which are consistent with the results presented in Figs 7–9. In addition, σ'' spectra for both fresh and biodegraded oil-wet samples display well-defined relaxation peaks centred at 10 Hz (Fig. 10). The addition of 1 per cent asphaltene to both fresh and biodegraded oil-wet samples (filled symbols) increased the magnitudes of σ' and σ'' (Fig. 10). At 10 Hz, the addition of asphaltene to fresh oil increases the magnitude of the

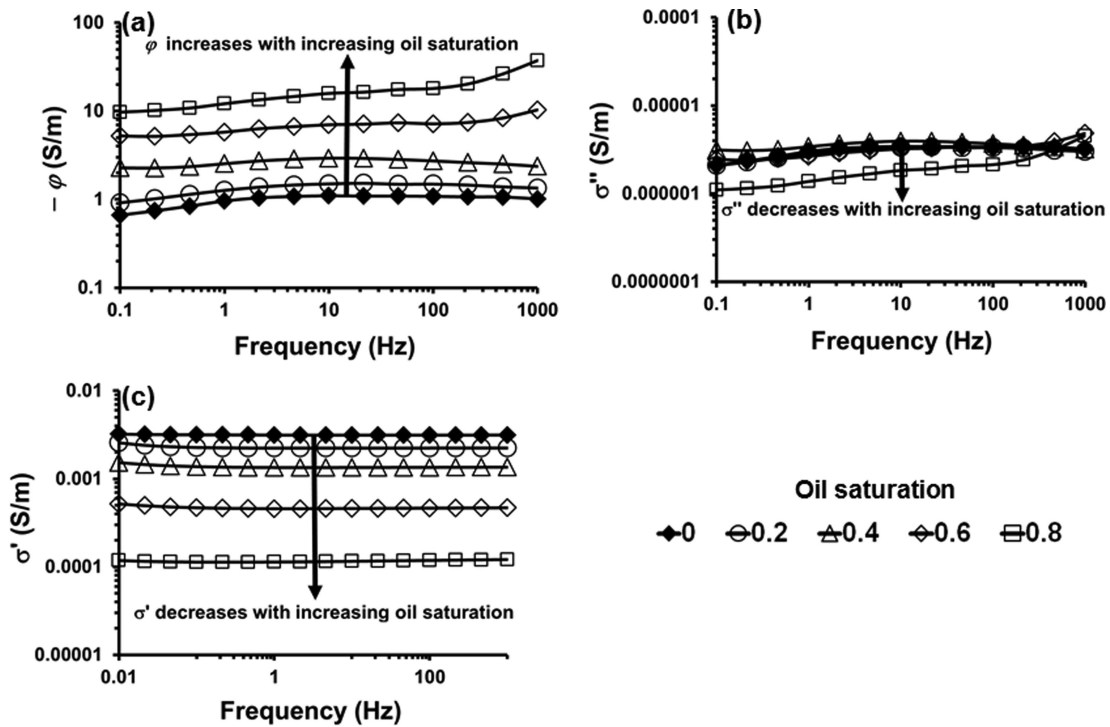


Figure 7. SIP results (a) phase (φ), (b) imaginary conductivity (σ'') and (c) real conductivity (σ') of oil-wet sand partially saturated with fresh oil. Absolute values of φ increased with increasing oil saturation whereas both σ'' and σ' decreased. Both φ and σ'' spectra show well-defined relaxation peaks at frequencies below 100 Hz.

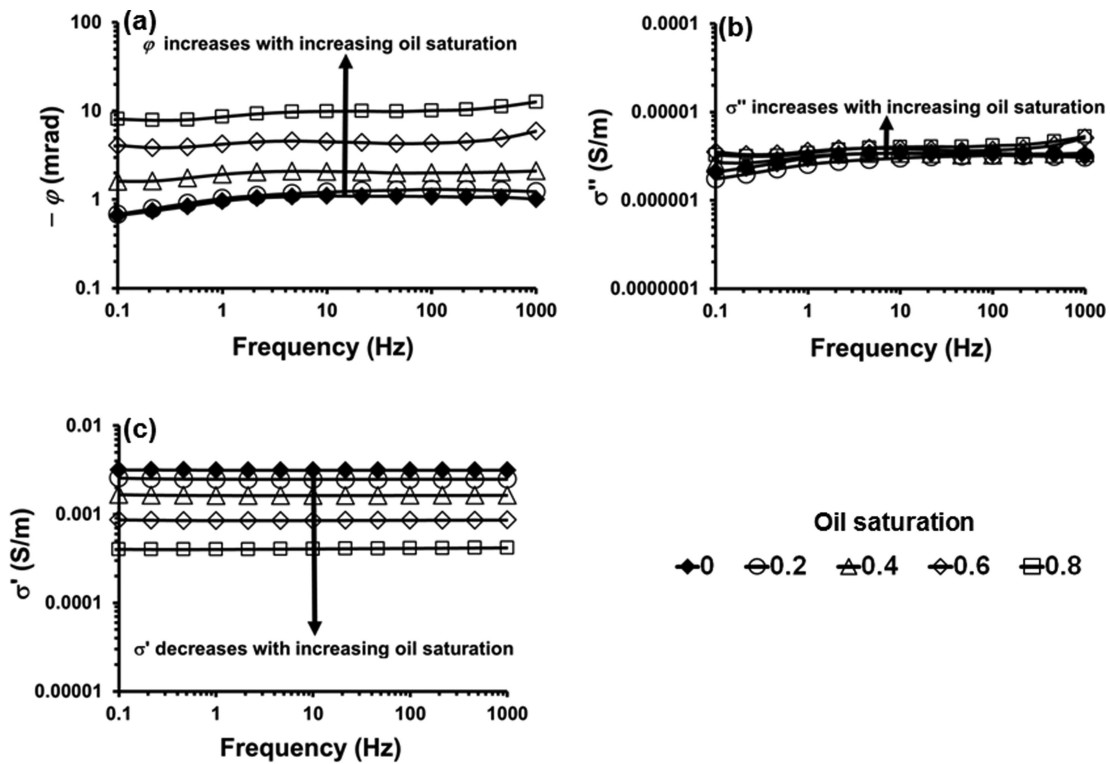


Figure 8. SIP results (a) phase (φ), (b) imaginary conductivity (σ'') and (c) real conductivity (σ') of oil-wet sand partially saturated with biodegraded oil. Absolute values of φ and σ'' increased with increasing oil saturation whereas both σ' decreased. Both φ and σ'' spectra show well-defined relaxation peaks at frequencies below 100 Hz.

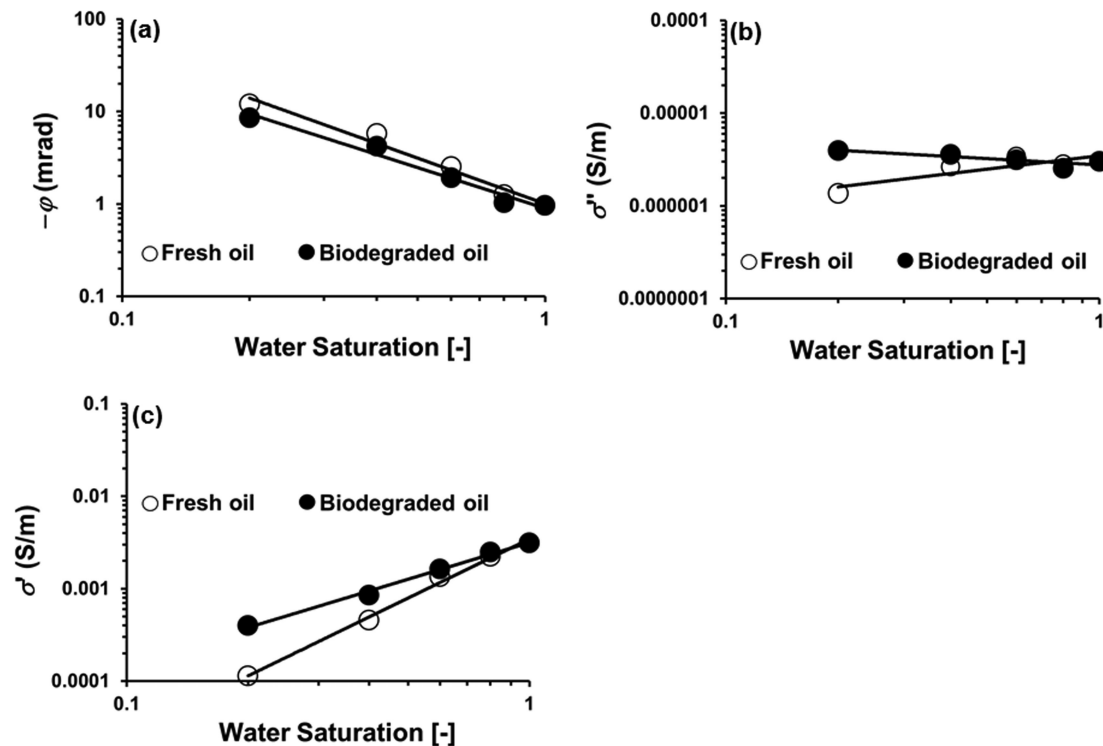


Figure 9. SIP results at 10 Hz (a) phase (ϕ), (b) imaginary conductivity (σ'') and (c) real conductivity (σ') of water-wet sand partially saturated with fresh oil (open circles) and biodegraded oil (filled circles) with solid trend lines as guide to the eyes. σ'' and σ' magnitudes of biodegraded oil-wet samples are higher than fresh oil-wet samples (at $S_w \leq 0.6$). In the case of biodegraded oil-wet samples, σ'' increased with increasing oil saturation/decreasing water saturation.

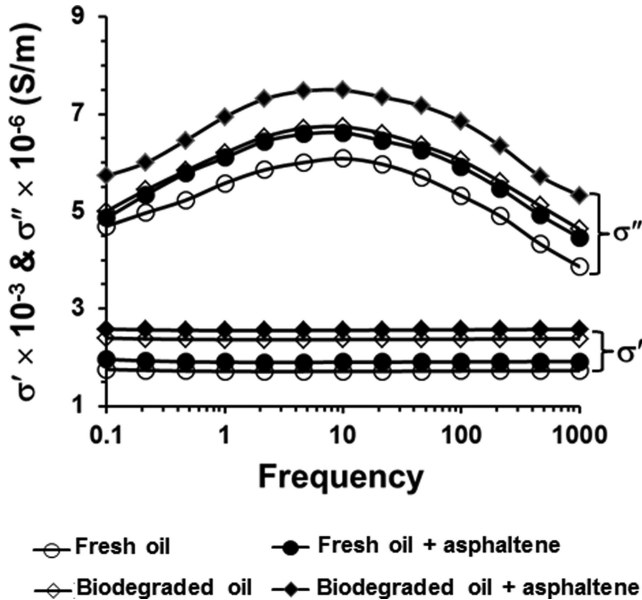


Figure 10. The imaginary (σ'') and real (σ') conductivities of fresh and biodegraded oil-wet sands (50 percent oil saturation) with and without 1 percent asphaltene. The addition of asphaltene enhanced σ' and σ'' components with biodegraded oil showing the highest magnitude.

σ' by 9.8 per cent from $1.71 \times 10^{-3} \text{ S m}^{-1}$ to $1.90 \times 10^{-3} \text{ S m}^{-1}$, whereas σ'' increased by 7.58 per cent from $5.58 \times 10^{-6} \text{ S m}^{-1}$ to $6.04 \times 10^{-6} \text{ S m}^{-1}$. On the other hand, the addition of asphaltene to biodegraded oil increases the magnitude of σ' by 7.35 per cent from $2.37 \times 10^{-3} \text{ S m}^{-1}$ to $2.55 \times 10^{-3} \text{ S m}^{-1}$, whereas σ'' increased

by 12.46 per cent from $6.08 \times 10^{-6} \text{ S m}^{-1}$ to $6.94 \times 10^{-6} \text{ S m}^{-1}$. The imaginary conductivity (σ'') magnitude of fresh oil-wet sample with asphaltene is shown to be nearly the same as the biodegraded oil-wet sample without asphaltene (Fig. 10).

5 DISCUSSION

Hydrocarbon contaminated sites are inherently complex due to hydrologic, lithologic and biogeochemical processes affecting the contaminant mass (Atekwana & Atekwana 2010). These processes also affect the wetting phase of the fluids filling the pores. For example, the oxidation–reduction mechanism associated with biogeochemical processes can alter the surface charge of the subsurface environments and the adsorption of crude oil polar components (e.g. asphaltene and resins) causing wettability alteration (Wang & Guidry 1994). Thus, in field settings, the geometric and volumetric distribution of the wetting and non-wetting phases in addition to the interfacial electrical properties at the solid–fluid and fluid–fluid interfaces may have an effect on the overall measured electrical properties of the hydrocarbon impacted sediments. Several mechanisms have been proposed to explain the enhanced electrical response observed at many hydrocarbon contaminated sites undergoing biodegradation (Sauck *et al.* 1998; Atekwana *et al.* 2000, 2002, 2004; Godio & Naldi 2003; Shevnin *et al.* 2003; Werkema *et al.* 2003; Abdel Aal *et al.* 2004, 2006; Frohlich *et al.* 2008). However, the contribution of biodegraded oil has not been investigated. Oil with high polar components resulting from the biodegradation process results in an enhancement in the conduction and polarization response compared to fresh oil only when oil is the wetting phase and at higher oil saturation.

5.1 Effect of saturation and wetting phase

The SIP results of water-wet sands partially saturated with biodegraded and fresh oil (Figs 4–6) showed no significant difference in the IP parameters as both oil samples displayed an increase in the magnitude of the phase (φ) and decrease in the magnitudes of the real (σ') and imaginary (σ'') conductivity components with increasing oil saturation. These results are in agreement with similar laboratory observations obtained by Schmutz *et al.* (2010) using fresh oil as non-wetting phase. Here, we suggest the magnitude of σ'' and σ' is most likely controlled by the conduction and polarization of the electric double layer (EDL) at the grain–water interface and the surface area to pore volume (S/V_{pore}) of the water-wetted interface. However, the effect of interfacial electrical properties of the water–oil interface may have minimal contribution to the IP response of the water-wetted sands partially saturated with fresh and biodegraded oil. The decrease in the magnitude of σ' and σ'' can be explained by the replacement of the conductive water phase responsible for the EDL polarization as well as the loss of its continuity with increasing oil saturation. Phase angle φ is a relative measure and depends on the magnitude of σ' and σ'' components. The increase in the magnitude of φ with increasing oil saturation is due to the much greater decrease in conduction represented by σ' compared to polarization represented by σ'' . Cassiani *et al.* (2009) showed results where spectral parameters (e.g. time constant, τ) for SIP measurements increased with the increase in saturation of non-aqueous phase liquids (octanol) of water-wet samples. Similarly, in a field investigation using SIP to delineate areas of different BTEX (benzene, toluene, ethyl benzene and xylene) concentrations, Flores Orozco *et al.* (2012) reported moderate increase in the polarization effect with increasing BTEX concentrations, for BTEX concentrations below the saturation concentrations (~ 1.7 g/l), followed by an abrupt decrease in the polarization effect for higher BTEX concentrations (> 1.7 g/l). However, the authors observed a general increase in the median relaxation time (τ_{50}) with increasing BTEX concentration. Based on the strong correlation between τ and contaminant concentration, the authors in both studies (Cassiani *et al.* 2009; Flores Orozco *et al.* 2012) explained the observation as resulting from the pore obstruction by the electrically non-conductive liquids and not exclusively due to the electrochemical effects at the grain–electrolyte interface. It is possible that the pore constriction effect on SIP response may exist in our samples with increasing oil saturation. However our results suggest that this effect is small and could possibly be masked by the strong conduction and polarization of EDL at the mineral–fluid interface. On the other hand, the SIP response observed by Cassiani *et al.* (2009) and Flores Orozco *et al.* (2012) may possibly be explained by the physiochemical properties of the non-aqueous phase liquid (octanol and BTEX) which are considered to be relatively more conductive than the crude oil used in our experiment. Additionally, the experimental procedure followed by Cassiani *et al.* (2009) during the drainage steps may have allowed for the interaction between the octanol and grain mineral surfaces which can affect and alter the IP response as observed by the study of Schwartz *et al.* (2012). The study by Schwartz *et al.* (2012) was conducted in unsaturated porous media contaminated with organic contaminants (diesel fuel and motor oil) and they observed an increase in the real part of the complex conductivity when air was replaced by the organic contaminants. They suggested that the increase in the real conductivity resulted from the adsorption of polar compounds contained in the organic contaminants to the mineral surfaces leading to the release of the inorganic ions into the pore water. The field results by Flores Orozco *et al.* (2012) are

site specific and do not consider the effect of other contaminants at the site. In addition, Flores Orozco *et al.* (2012) did not provide information regarding the wettability conditions prevailing at the site, which would be more complex, compared to our simple experimental setup.

Our results also show that the σ' saturation exponent (n) for the fresh oil (1.432) is relatively higher than biodegraded oil (1.283) which indicates that fresh oil is more water repellent than biodegraded oil. Moreover, σ'' saturation exponents (p) do not follow the relationship ($p = n - 1$) similar to the observation obtained by Schmutz *et al.* (2012) in water-wet sands partially saturated with different oil types indicating that this relationship is not universal.

5.2 The role of asphaltene

Several studies have demonstrated the importance of the electrical properties of asphaltenes and their effect on the overall electrical properties of crude oil (Lichaa & Herrera 1975; Fotland *et al.* 1993; Fotland & Anfindsen 1998; Friisø *et al.* 1998; Hasnaoui *et al.* 1998; Rejon *et al.* 2004; Sheu & Acevedo 2006; Goual 2009). In an attempt to explain the IP results of oil-wet sand using oil samples with high asphaltene percentage (20 per cent), Revil *et al.* (2011) hypothesized that the IP response may result from the cation exchange capacity associated with the presence of a polar component at the oil–water interface. Our results with oil-wet sands and the effect of adding 1 per cent asphaltene to fresh and biodegraded oil provide evidence to support this hypothesis. Our results show that when oil is the wetting phase, there was a notable difference in the magnitude of the IP parameters between the fresh and biodegraded oil in contrast to the results with the water-wet case. The magnitude of σ'' and σ' for the biodegraded oil-wet sands were relatively higher compared to fresh oil-wet sands at oil saturation greater than 40 per cent (Fig. 9). The biodegraded oil has a higher percentage of asphaltene (16 per cent) compared to fresh oil (9 per cent). Controlled laboratory experiments with fresh and biodegraded oil-wet sand showed that the addition of 1 per cent asphaltene enhanced σ' and σ'' with biodegraded oil showing the highest magnitude (Fig. 10). The results also show that the addition of asphaltene has a greater impact on σ' of biodegraded oil-wet samples (12.46 per cent) than fresh oil-wet samples (7.58 per cent). Previous studies have documented that the dipolar asphaltene fractions in crude oils are interfacially active and are capable of building strong and rigid films at a water and oil interface (Schildberg *et al.* 1999; Fordedal *et al.* 1996). Despite the fact that we did not investigate the presence of such conductive film in our samples, we propose that having such conductive film of asphaltene at the mineral–oil and oil–water interfaces would potentially enhance the conduction and polarization of the oil-wet sand when an electric field is applied. At the oil–water interface, the adsorbed asphaltene film can create a surface charge resulting from the ionization and complexation of the functional groups in asphaltene (e.g. carboxylic, hydroxyl, ether, ester, aldehyde, ketone, amine and amide) at the interface. This surface charge will be compensated by the specific adsorption of the counterions in water, creating an EDL at the interface (Szymula *et al.* 2000). This EDL can be polarized when an electric field is applied. Also, the asphaltene film will enhance the conduction due to the increase in the cation exchange capacity at the oil–water interface. Chow *et al.* (2004) measured the dielectric response and conductivity of different bitumen fractions in solution for a wide range of concentrations at a single frequency (1000 Hz). They concluded that asphaltenes were the main

constituents of the bitumens that determined their conductivity, while the dielectric response was affected by all polar constituents.

Pore constriction may also be considered as another source of IP enhancement particularly at higher oil saturation as observed in our results. The adsorption of asphaltene on charged mineral surfaces could be considered as adsorption of ionic surfactants (McLean & Kilpatrick 1997; Schorling *et al.* 1999). The adsorption of asphaltene on mineral surfaces can possibly contribute to the IP response by the dipolar polarization usually associated with the orientation of permanent dipoles in asphaltenes (Tjomsland *et al.* 1996; Evdokimov & Eliseev 2001). Nevertheless, the exact source mechanism at the mineral-oil and oil-water interfaces require further investigation in order to provide a full theoretical understanding.

5.3 Possible IP source mechanisms

Based on our results, a schematic diagram is provided that summarizes the possible IP source mechanisms that can be integrate and associate with biodegraded oil in porous media as wetting and non-wetting phase (Fig. 11). When water is the wetting phase and sand partially saturated with non-wetting oil, three different IP source mechanisms may occur (Fig. 11a). The most likely and preferred IP source mechanism will be associated with conduction and polarization of the EDL at the mineral-water interface where water (conductive phase) forms a continuous film coating the sand grain (Fig. 11a-1). The second possible IP source mechanisms may result from the pore constriction and charge separation at high oil saturation (Fig. 11a-2). The third IP source mechanism may arise from the possible formation of EDL at the water-oil interface resulting from the adsorbed conductive film of asphaltene and the creation of a net surface charge compensated by counterions in water (Fig. 11a-3). We hypothesize that the effect of the second and third IP source mechanisms could be small compared to the conduction and polarization of the EDL at the mineral-water interface which is favoured by the conductive phase of water coating the mineral grain surfaces.

Similarly, when oil is the wetting phase, three different IP source mechanisms are proposed but with different geometric and volumetric locations (Fig. 11b). Here, the most favourable IP source mechanism may arise from the conduction and polarization of the EDL formed at the oil-water interface resulting from the ionization and complexation of adsorbed film asphaltene rich in polar function groups (Fig. 11b-1). The second IP source mechanism is related to the pore constriction at high oil saturation and its contri-

bution could be higher than the one with water-wet case because it is favoured by the presence of the conductive phase (water) filling the pore space (Fig. 11b-2). The third IP source mechanism is related to the dipolar polarization of permanent dipole moments (e.g. sulphur, nitrogen, oxygen, nickel and vanadium) located within the adsorbed asphaltene layer at the mineral grain surfaces (Fig. 11b-3). However, the mentioned IP source mechanisms at the water-oil interface (water-wet case) and mineral-oil interface (oil-wet case) require further laboratory and theoretical studies to develop a fundamental understanding of how the properties of these interfaces in terms of interfacial area and pore-scale distribution of fluids would contribute to the electrical properties of porous media.

6 CONCLUDING REMARKS

This study provides insights into the contribution of biodegraded oil to the SIP response of porous media at different wetting and saturation conditions and demonstrates the importance of polar components in crude oil (e.g. asphaltene) in affecting the SIP response. Our laboratory results show that biodegraded oil with high polar components (e.g. asphaltene) resulting from the biodegradation process showed an enhancement in the conduction and polarization response compared to fresh oil only when oil is the wetting phase and at higher oil saturation. The polar components of biodegraded oil represented by the asphaltene fractions with their ionization and complexation reactions at interfaces play an important role in the observed IP response of biodegraded oil. The enhancement in IP response (σ'' in particular) of biodegraded oil-wet samples may possibly result from integration of different and multiple source mechanisms such as the conduction and polarization of EDL at oil-water interface, pore constriction at high oil saturation and possibly dipolar polarization of permanent dipole moments (e.g. sulphur, nitrogen, oxygen, nickel and vanadium) located within the adsorbed asphaltene layer at the mineral grain surfaces. The insignificant difference in IP response between fresh and biodegraded oil when water is the wetting phase may possibly be attributed to the strong and favourable IP source mechanism associated with the conduction and polarization of EDL at the mineral-water interface. The elevated electrical conductivity and IP response observed at several aged hydrocarbon contaminated sites undergoing biodegradation are partially related to the biogeochemical changes in oil composition (e.g. increase in polar components) and possible alteration of wettability conditions from water-wet to oil-wet. The results of our study may have implications

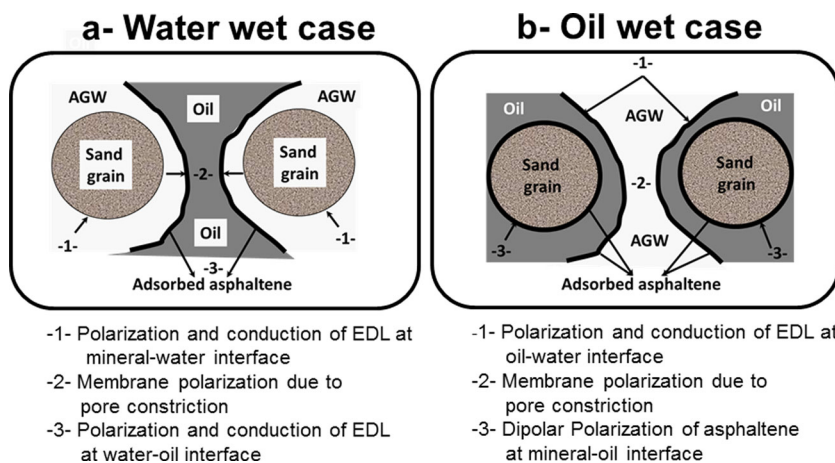


Figure 11. Schematic diagram showing the different possible SIP source mechanisms for (a) water-wet case and (b) oil-wet case, using fresh and biodegraded oil.

for the successful interpretation of SIP data from oil spill sites as well as electrical data from reservoirs with oil at different states of biodegradation. In particular our results show that the σ'' can be used to track wettability alteration (water-wet to oil-wet and vice versa) and therefore can successfully be used in microbial enhanced oil recovery studies. Further studies are required to investigate the effect of other components in crude oil such as resins, trace metals, biogenic metallic minerals (e.g. magnetite) and organic acids on the SIP response of porous media.

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