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Title

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Abstract

It is well-accepted that Archie's law is only applicable to "clean" rocks and soils but fails in "dirty" ones where clay minerals possess an additional component of surface conductivity. Although several models, e.g., Waxman-Smits model, were presented to account for this phenomenon, surface conductivity is always inappropriately treated as constant, which actually only holds at high salinities. The essential non-linear characteristic differing over fluid salinities has not been physically or mathematically explained well in those models. We scrutinize the conduction mechanism of clayey rocks and soils and ascribe this non-linear feature to (i) variation of the electrical double layer and (ii) the intrinsic clay-and-water conduction pattern. With effective medium theory, we develop an easy-to-use non-linear model that both reflects electrochemical theories and explains the measurement data well. Our model can be used to produce more accurate results for laboratory- and field-scale petrophysical parameter evaluations than the previous models.

Key Points

- ✧ Conductivity of clayey rocks and soils manifests an obvious non-linear behavior with respect to changes of the pore water salinity

- ✧ Non-linear conductivity is resulting from (i) variation of electrical double layer and (ii) the intrinsic clay-and-water conduction path

- ✧ Our non-linear model reflects electrochemical theories, explains measured data well, and is very easy-to-use

Plain Language Summary

Electrical and electromagnetic methods are commonly-used hydrogeophysical methods for large-scale non-invasive subsurface investigations, where different conductivities between Earth materials lay their foundations. Unfortunately, for rocks and soils with clay minerals, their conductivities behave non-linearly with the pore water. Inappropriately using Archie's law or other linear models could lead to erroneous rock/soil parameter estimation or field data interpretation. Here we develop an easy-to-use non-linear model which would produce more quantitative petrophysical and geological results from measured geophysical data, e.g., more accurate porosity assessment and lithological discrimination.

1 Introduction

Electrical conductivity of different rocks and soils lays the base for electrical logging and electrical and electromagnetic (E&EM) methods that have been extensively used for near-surface, environmental, and hydrogeological investigations (e.g., Chelidze & Gueguen 1999; Chelidze et al., 1999; Glover 2015). It is the pioneering work of Archie (1942) that makes the quantitative assessment of porosity available and paves the way for other petrophysical parameters. Several years later, Patnode & Wyllie (1950) found that Archie's law is only suitable to "clean" samples as clayey minerals in the "dirty" ones present themselves as "conductive solids". Winsauer & McCardell (1953) ascribed the clay conductivity to its electrical double layer (EDL) for the first time. Thus the additional component Patnode & Wyllie (1950) added to Archie's law shall be called the surface conductivity. Soon after, Wyllie & Southwick (1954) discovered that the surface conductivity is not constant but differs at low and intermediate salinities, and they

presented a three-resistor (TR) model to explain this non-linearity. It shall be clarified here that "cleanness" and "dirtiness" are relative terminologies that are essentially a question of the ratio between surface and pore water conductivity (i.e., the Dukhin number. c.f., Shilov et al., 2001). Indeed, one can find surface conductivity even in clean glass beads (e.g., Bolève et al., 2007).

Although research on the electrical conductivity of clayey rocks and soils progressed significantly in the 1950s, the following years are not always the case. Despite the fact many models have been presented to account for this non-linear characteristic, they are argued not to comply with electrochemical theories or not coincide with measurements, and most are too complex to use (Bussian, 1983). For example, the TR model (Wyllie & Southwick, 1954) can explain measurements well, yet it is exclusive of EDL, clay minerals being treated as classic conductors. The Waxman-Smits (WS) model (Waxman & Smits, 1968), probably the most popular model, postulates that the ionic mobility decreases with the diminishing ionic concertation which is opposite to the electrochemical theory (e.g., Bockris & Reddy, 1998). The Padé approximant (PA) model (Schwartz et al., 1989) first calculates the low-salinity conductivity with surface tortuosity and the high-salinity conductivity with bulk tortuosity, respectively, then 'stitches' these two together with a Padé approximant. The former does have a physical basis, yet the latter is purely mathematical. The Bruggeman-Hanai-Sen (BHS) model wholly uses the differential effective medium (DEM) theory to derive its equation (Sen et al., 1981). While Poisson's equation can be seen as its physical basis, this model treats the clay minerals as conductive solids and never considers the EDL variation with salinities. Besides, this model gives an implicit equation and only has closed-form expressions under some approximations (Bussian, 1983).

We recognize that a model quantitatively accounting for such non-linearity is very imperative to petrophysical and geophysical communities. For instance, in the laboratory, using the linear equation to fit a clayey rock sample's bulk conductivity tends to underestimate its formation factor if data belonging to the non-linear portion are contained in such a linear curve fitting. Similarly, in the field, when E&EM methods are used in the critical zone studies, the fresh pore water often makes the bulk conductivity of clayey soils lie in its non-linear portion. The linear model could output erroneous hydraulic parameters in this situation. With the increasing usage of E&EM tools for critical zone research, it is important to better understand this non-linear behavior. Using the effective medium theory, we obtain an easy-to-use non-linear model that is well-aligned with both electrochemical theories and measurements. Our model is expected to produce better results than the previous models, especially in the circumstances of freshwater or high clay minerals.
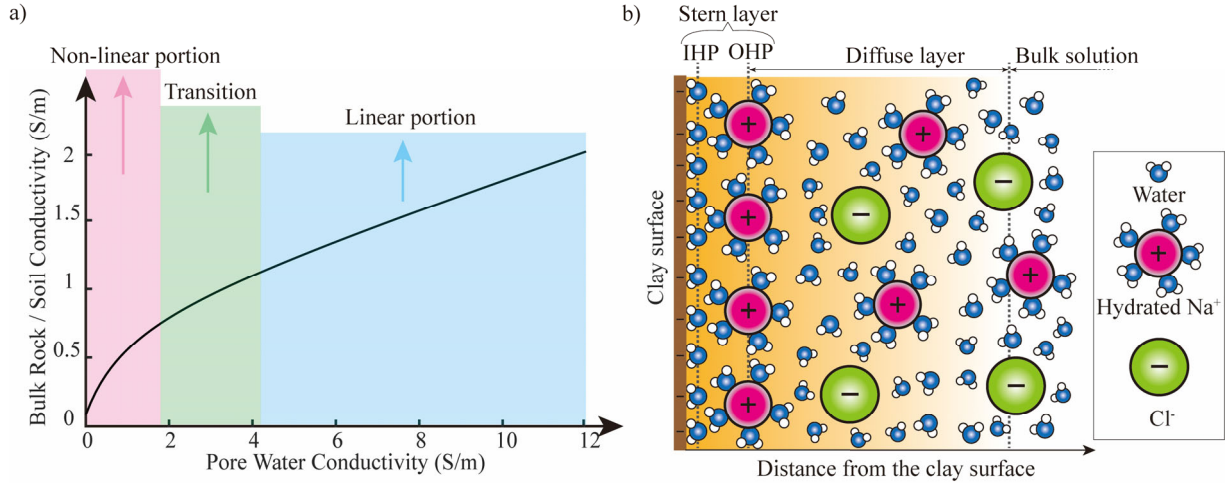
2 Model development

Figure 1. Schematic demonstration of clay conductivity curve and its EDL structure. (a) shows a typical conductivity curve of clayey rock/soil. Differences between clayey rocks and soils are mainly in their formation factors here (i.e., the slope of the linear portion). Note that conductivity values are just for an example here and they are actually sample-dependent; (b) demonstrates the EDL structure around the clay surface. The faded yellow background signifies that the potential decreases with the distance from the clay surface. Note that, different to Na^+, almost none water molecules are attached to Cl^- because of its bigger ion size (c.f., Bockris & Reddy, 1998).

Figure 1a gives the typical bulk conductivity curve shape of clayey rocks and soils, which shows three features: (I) The curve neither crosses the origin nor shows such a trend; (II) At high salinity (i.e., the linear portion), the bulk conductivity σ is linear with the fluid conductivity σ_w, (III) At low and intermediate salinities (i.e., the non-linear portion and the transition, respectively), the bulk conductivity behaves non-linearly to the fluid conductivity.

Feature (I) nullifies Archie's law for clayey rocks and soils, while feature (II) ratifies the PW model (Patnode & Wyllie, 1950) that adds constant surface conductivity σ_s to Archie's law at high salinity. Nevertheless, feature (III) specifies that σ_s increases concavely when the salinity grows. Considering this growth runs smoothly, it is mathematically deducible that the PW model still holds its form but σ_s becomes a function of σ_w as

$$\sigma = \frac{\sigma_w}{F} + \sigma_s\left(\sigma_w\right), \tag{1}$$

where the first term is Archie's law and F the formation factor, while the second is the fluid-dependent surface conductivity. Obviously, clay minerals cause this concave non-linearity in Eq. (1). To derive the effect of pore fluid salinity on surface conduction, we will investigate the principles of EDL and the role they play in $\sigma_s\left(\sigma_w\right)$.

2.1 Electrical double layer (EDL): Structure and variation

Clays are not the most abundant components compared to feldspars in the Earth's crust, but the most abundant natural reactive solids on the Earth's surface (Schroeder, 2018). The presence of clay minerals can be in a consolidated form of clayey rocks (e.g., shale) or unconsolidated clayey soils (e.g., bentonite). The strong clay reactivity stems from its two basic characteristics: high surface area and net negative surface charges. The former results from its extremely small size ($< 2\,\mu m$) and the latter from its special chemical structure. Clay minerals are hydrous

aluminum phyllosilicates made of two fundamental fractals of the tetrahedral sheet between O^{2-} and Si^{4+} and octahedral sheet between OH^- and Al^{3+} (or Mg^{2+} with isomorphous substitution). This special chemical structure induces net negative charges on clay surfaces and interlayers. Though permanently charged, clay minerals in the dry state are not conductive as these charges are fixed which is completely different from metals (Winsauer & McCardell, 1953).

However, when dry clay minerals transit into a wet state with ionic solutions, it becomes conductive. This is due to the establishment of the EDL on a clay particle's surface with mobile charges when exposed to a saline solution as shown in Figure 1b (Bockris et al., 2000). Nearest to the clay surface, there is always a hydration sheath because of the strong polarization of water molecules. These water molecules flop down their orientations for the electrical force from the charged surface. The second row is largely reserved for solvated cations whose locus is called the outer Helmholtz plane (OHP). The first hydration sheath (sometimes accompanying with specifically adsorbed ions, the locus of which is called the inner Helmholtz plane, i.e., IHP) and the second row of solvated cations are together named as the Stern layer. Outside the Stern layer, the electric force and thermal jostling both take effect, which leads to a mixture of hydrated cations and anions (i.e., the diffuse layer). Beyond the diffuse layer, it is the bulk solution where thermal buffeting dominates (Bockris et al., 2000).

It is axiomatic that the conduction of a clay particle is via its EDL. Unfortunately, EDL is not static but dynamic. Amongst its influencing factors, fluid salinity is the most encountered one. Electrochemical experiments prove the existence of a critical salinity above which the clay particle's conductivity σ_{cp} can be seen as constant (Zukoski & Saville, 1986b). From EDL theories, the thickness of the diffuse layer (i.e., the Debye length) shrinks with the increase of salinities and thus increase σ_{cp} until its growth is negligible, while some believe that the EDL conduction is mostly from the Stern layer rather than the diffuse layer (Zukoski & Saville, 1986a). Dynamic Stern layer model depicts the constant σ_{cp} as the full saturation of cations in its Stern layer with the salinity increase (Zukoski & Saville, 1986a, b). A debate between dynamic diffuse and Stern layer models is beyond the scope of our paper as they both evidence that the critical salinity for the constant σ_{cp} is extremely low which certainly cannot explain the concave non-linearity in Figure 1a (Bernabé & Revil, 1995). It is self-evident that there is another mechanism more dominant than the EDL variation that controls the whole non-linearity. In this context, it appears prudent to avoid taking such EDL variation so strictly and to focus on the main dominator for this non-linearity. It is practical to average this effect to exclude its steep changes (i.e., use the mean value of σ_{cp} with salinities), which is acceptable as both theories and experiments confirm EDL variations happen merely near zero salinity (Zukoski & Saville, 1986a, b). Considering that distilled or de-ionized water is hardly met in geophysical circumstances, such an averaging scheme, albeit it may overestimate σ_{cp} near zero conductivity, can help us focus on the main non-linear mechanism without sacrificing our model's applicability.

2.2 Clay-and-water conduction path: Effective medium theory (EMT)

In nature, clay particles mostly present themselves as disseminated clay aggregates or massive streaks in rocks and soils which can be categorized based on their clay fraction such as shales subdivides into dispersed, structural, and laminar ones. Although laminar shale is

considered to be a macroscale continuum, scanning electron microscopy (SEM) images show that scattered shale flakes exist widely (Schroeder, 2018). Thus when clayey rocks and soils are exposed to EM field, clay particles cannot conduct current hundred-percent via their interconnected EDLs, but through a path switching between EDL and bulk fluid (i.e., the clay-and-water pattern). Whilst some local, continuous EDL paths do exist, taking all the clay particles as a whole, it is still a clay-and-water conduction mechanism. One apparent excepting case might be compact pure clays at laboratory. However, because of possible colloid repulsion and rough surface curvatures, we still don't expect currents to transfer completely via interconnected EDLs. Recent laboratory measurements on pure clay validate that its real (not quadrature) conductivity also shows almost the same concave nonlinearity (Mendieta et al., 2021).

The geometry of clayey rocks and soils can be roughly illustrated in Figure 2a. It is self-explanatory that there are two main conduction paths within the pore: one through the centered bulk fluid (i.e., Path #1) and the other via the clay-and-water conduction path clinging to the pore wall (i.e., Path #2). These two paths statistically run parallel with each other with the former described as Archie's law and the latter the surface conductivity σ_s, which can be seen as the physical explanation for Eq. (1). A close-up of these two parallel conduction paths #1 and #2 are drawn in Figure 2b where the upper part represents the path of pore fluid and the lower is the clay-and-water conduction path. It is also well to bear in mind that "clay" in "clay-and-water" is actually clay's EDL because dry clay is almost insulating and "water" here specifically indicates clay's contiguous water clinging to the pore wall in such a conduction path (i.e., Path #2).
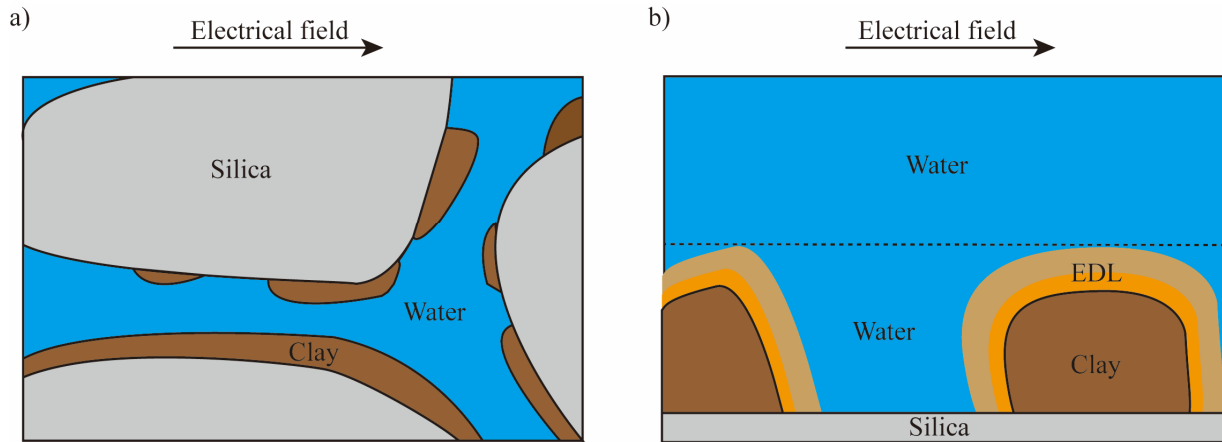

Figure 2. Schematic geometry of clayey rocks and soils. (a) and (b) are the overview and close-up of the two parallel conduction paths under electrical field, respectively.

To calculate σ_s, the clay-and-water path can be seen as a mixture of conductive clay and fluid. Since we have previously used the averaging scheme for the EDL variation to exclude its steep change around zero salinity, the conductivity of clays' EDL can be seen as from clay themselves during the mathematical derivation here. Regarding this mixture, the fluid water bears the conductivity σ_w and the clay σ_c. It must be stressed that the clay conductivity σ_c should not be confused with the aforementioned clay particle's conductivity σ_{cp}, albeit they do have correlations. For example, natural clayey rocks and soils usually contain more than one kind of clay mineral (e.g., kaolinite, illite, and smectite), different kinds of clay particles

inherently hold different σ_{cp}. Patchett (1975) presented one method to average σ_c out of σ_{cp} based on their mass fractions which worked well on experiments (e.g., Woodruff & Revil (2011), Dumont et al., 2021). Additionally, inorganic precipitation on a clay surface decreases its conductivity σ_{cp} (e.g., Wu et al., 2010). Thus σ_c represent the average conduction abilities of all the σ_{cp} (i.e., the averaging scheme), which is certainly rock- and soil-dependent because of many influencing factors like clay type, clay fraction, clay aggregation extent, etc.

From Figure 2b, the surface conductivity σ_s represents the effective conductivity of this clay-and-water conduction path. We resort to the effective medium theory (EMT) to calculate σ_s out of σ_c and σ_w. Maxwell Garnett (MG) equation (Garnett, 1904) is employed here because of its simplicity yet broad applicability (Landauer, 1978)

$$\frac{\sigma_s - \sigma_c}{\sigma_s + 2\sigma_c} = \xi \frac{\sigma_w - \sigma_c}{\sigma_w + 2\sigma_c}, \tag{2}$$

where ξ is the water volume fraction in the clay-and-water conduction path that denotes the percentage of water participating in such a clay-and-water conduction pattern. Although some necessary geometrical approximation is postulated, it is underlined that MG equation is not a simple arithmetic mixing rule but a physics-based one where Maxwell's equations are used during its derivation. However, as a side note, MG equation is always incorrectly written as Maxwell-Garnett equation in the literature. Actually, J. C. Maxwell Garnett is the inventor of this equation who is an English physicist (1880-1958), while the founder of Maxwell's equations is the Scottish physicist James Clark Maxwell (1831-1879). J. C. Maxwell Garnett's father William Garnett used to serve as JC Maxwell's laboratory demonstrator and put J. C. Maxwell as his son's given name for respect (c.f., Landauer, 1978). It should also be stressed that in the MG equation, the contributions of clay and water are not identical, and one must be chosen as the matrix (i.e., the host) and the other as inclusion (i.e., the guest). Mathematically speaking, σ_c and σ_w are not symmetrical to each other in Eq. (2). From a physical perspective, for the surface conductivity σ_s, as its self-explanatory name, clay plays a more characteristic role than water through the surface tortuosity (Schwartz et al., 1989), which leads to the fact that clay must be chosen as the matrix and water as the inclusion. From Eq. (2), we can directly derive the surface conductivity

$$\sigma_s = \frac{(2\xi + 1)\sigma_c \sigma_w + 2(1 - \xi)\sigma_c^2}{(2 + \xi)\sigma_c + (1 - \xi)\sigma_w}. \tag{3}$$

Given path #1 and #2 run parallel to each other (Figure 2), with Eq. (1) and (3), our non-linear model is presented as

$$\sigma = \frac{\sigma_w}{F} + \frac{(2\xi + 1)\sigma_c \sigma_w + 2(1 - \xi)\sigma_c^2}{(2 + \xi)\sigma_c + (1 - \xi)\sigma_w}. \tag{4}$$

It can be shown that this new non-linear model has a very simple form with the first term as the classic Archie's law and the second as the clay- and fluid-dependent surface conductivity $\sigma_s(\sigma_w, \sigma_c)$ with ξ balances its two contributors. It can be easily tested that our model holds a non-linear concavity with the increase of σ_w when σ_w and σ_c are comparable (i.e., at low or intermediate salinity) and becomes linear to σ_w at high salinities. At high salinity (i.e., in the linear portion), σ_s reaches its constant maximum as

$$\sigma_s^{max} = \frac{2\xi + 1}{1 - \xi} \sigma_c. \tag{5}$$

We proceed to validate our model on natural and synthetic circumstances.

3 Model verification

3.1 Natural clayey rocks and soils

The non-linear surface conductivity has been studied for 70 years since this additional term was first discovered by Patnode & Wyllie (1950), which accumulates extensive high-quality data to test our models. We successfully verified our model on these available data and four examples are shown here.
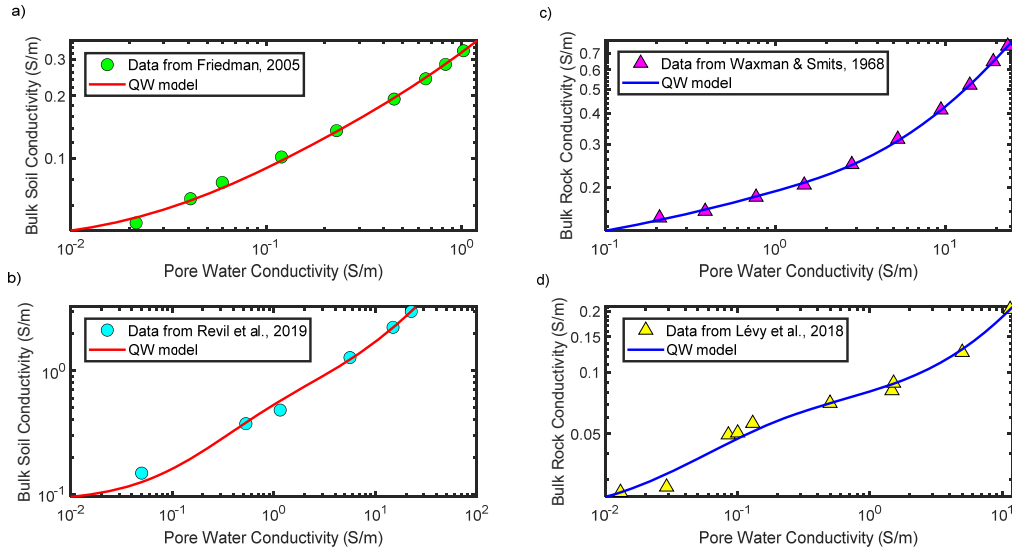
Figure 3. Model verification on natural clayey soils and rocks. Data sources are displayed in the respective inserts where QW model, by convention, represents our developed non-linear model. Note that this plot is in log-log scale.

Two clayey soils in Figure 3a and 3b are the Sample Bonsall-B from Friedman (2005) and AE from Revil et al. (2019), respectively, and two clayey rocks in Figure 3c and 3d are the Sample #26 from Waxman & Smits (1968) and L31 from Lévy et al. (2018), respectively. Our model fits all these 4 datasets extremely well with coefficient $R^2 > 0.99$. The parameters for soil Sample Bonsall-B are $F = 4.71$, $\sigma_c = 0.06$, and $\xi = 26.7\%$, and for Sample AE $F = 9.79$ $\sigma_c = 0.21$, and $\xi = 47.3\%$, while for the rock Sample #26 $F = 41.63$, $\sigma_c = 0.14$, and $\xi = 11.1\%$, and for Sample L31 $F = 88.03$, $\sigma_c = 0.03$, and $\xi = 30.3\%$. All these parameters are in accord with the investigations of the related literature.

It can be seen that our model is able to capture the non-linear and linear portions both very well. Considering $\sigma_s(\sigma_w)$ is always smaller than σ_s^{max}, simply using a linear model (i.e., PW model) always tends to under-predict the true formation factor F. Some may argue that this problem can be circumvented by kicking off the non-linear portion and only fitting the linear part. However, this method is not practical as the transition from nonlinearity to linearity cannot be precisely determined in many cases. The inclusion of some data points from the non-linear to linear transition zone will again result in an inaccurate F prediction. The necessity of including the non-linear portion is also underscored by these 4 datasets for freshwater conductivity ($< 0.2\,\mathrm{S/m}$) which is often encountered in nature, where empirical or petrophysical relationships

developed at high salinities do not apply to the freshwater situation and could lead to erroneous assessments.

Although these natural clayey rock and soil datasets have validated the applicability of our model. A caveat is that the parameter σ_c and ξ cannot be comparatively analyzed in these natural samples because of the large variations in formation factors, clay types, and clay contents. In the next chapter, an experiment using synthetic samples will be presented to illustrate this aspect.

3.2 Synthetic clay experiment

Synthetic samples have advantages over natural ones as their compositions can be qualitatively changed such that model parameters can be analyzed. Wyllie & Southwick (1954) already performed such an experiment. To keep the formation as identical as possible, a synthetic cation exchange material of polystyrene sulfonates named Amberlite is employed as they always keep their spherical shapes without dissolution in fluid as clay minerals. The experiment was designed as 4 cases: 1) Full glass spheres, 2) 60% volume of glass spheres and 40% Amberlite spheres, 3) 20% volume of glass spheres and 80% Amberlite spheres, and 4) 100% Amberlite spheres, where all the glass and Amberlite spheres are sieved and chosen to 40-50 mesh U.S. Sieve Series which leads to an approximate porosity of 40% for all the cases.

To test our model, it shall be noted that the full-glass case (i.e., clay-free situation) is a mathematical singular point for our model and the non-negative least squares (NNLS) method must be used for the regression, otherwise negative ξ might emerge. To make cases comparable, we denote $\xi = 100\%$ and $\sigma_c = 0.007\,\text{S/m}$ for this clay-free case, albeit NNLS outputs a near zero value for ξ because of singularity. All in all, as shown in Figure 4a, our model fits these 4 cases with $R^2 > 0.99$, yet we found a slight growth of root mean squared errors (RMSE) with the increase of Amberlite fraction. Considering goodness-of-fit statistics tend to conceal small values' effect, we checked the performance point by point. Interestingly, we found our model doesn't perform very well at those relatively extremely low salinities (e.g., 0.02 and 0.05 S/m for case #3 and #4, respectively) which are much clearer in the log-log scale in Figure 4b (note that $10^{-1.8}$ =0.016, $10^{-1.3}$ =0.05 S/m). It seems to have a trend of overestimation at such extremely low salinities with the increase of Amberlite. Looking back on our discussion on EDL variation, this is very reasonable because higher clay content leads to stronger EDL variations at extremely low salinities where our averaging scheme of constant σ_c might misrepresent these steep changes. Mathematically, a weighted least squares (WLS) method to decrease the importance of these extremely low salinities could output better results. To make things simple, here we neglect to fit the four extremely low salinity points (i.e., giving zero weight to them) for the full-Amberite case.
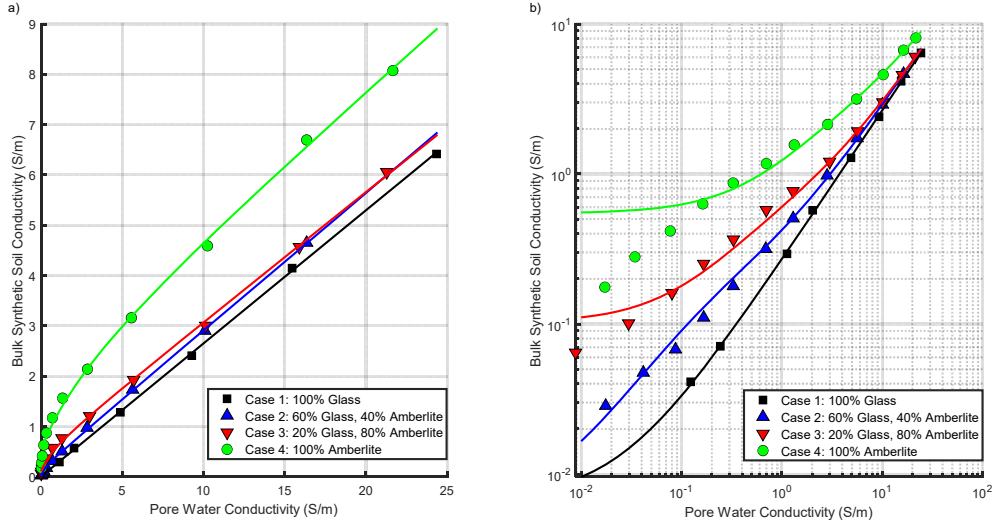
Figure 4. Model verification on synthetic clayey soils with the case constitutions in the lower insert. To respect both large and small values, data are plotted in normal and log-log scales in (a) and (b), respectively.

With the same case order, we obtain the model parameters as F = 3.79, 3.66, 3.88, and 3.55; σ_c = 0.007, 0.024, 0.191, and 0.929 S/m; ξ = 100%, 68.4%, 36.4%, and 31.8%. Using Eq. (5), we can also get σ_s^{max} = 0.007, 0.181, 0.518, 2.23 S/m. The similar F is the result of the identical porosity at about 40% for these glass/Amberlite spheres (c.f., Friedman, 2005). The obvious increase of σ_c and the decrease of ξ with the increasing Amberlite content are in complete accord with our analysis of the clay-and-water conduction path which states that both clay and water involve in this conduction path and a higher clay content will increase the clay conductivity σ_c and tend to decrease the participating role of water (i.e., decrease ξ). Besides, the increasing trend of σ_s^{max} justifies the well-received conclusion that surface conductivity can be used as an index for clay content. One interesting thing shown here is that σ_c manifests more sensitivity than σ_s^{max}, which probably hints that σ_c might be a better indicator for clay content. However, this needs a further quantitative study.

4 Discussions with other models

Here we briefly compare our model with two extant models: TR (Wyllie & Southwick, 1954; Lévy et al., 2018) and BHS (Sen et al., 1981; Bussian 1983). TR model is

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3$$
$$= \frac{\sigma_w}{F} + \frac{\sigma_c \sigma_w}{x\sigma_c + y\sigma_w} + \frac{\sigma_c}{z}$$
$$= \frac{\sigma_w}{F} + \frac{(y+z)\sigma_c \sigma_w + x\sigma_c^2}{xz\sigma_c + yz\sigma_w} \tag{6}$$

where σ_1, σ_2, and σ_3 denote three resistors of bulk fluid, clay-and-water series, and continuous clay, and x, y, and z are empirical geometric factors. Mathematically, it is not surprising TR model works well on clayey rocks and soils as its redundant parameters x, y, and z can be written as the elementary functions of our ξ as

$$x = \frac{(\xi+2)^2}{9\xi}, \quad y = \frac{(\xi+2)(1-\xi)}{9\xi}, \text{ and } z = \frac{\xi+2}{2(1-\xi)} . \tag{7}$$

Physically, our ξ explains the meaning of these three empirical factors. If derivations are compared, it can be seen that the mathematical-physical simplicity of our model is from the appropriate employment of EMT. For geomaterials interacting with the E&EM field, lumped circuit theory is not a reasonable representation as geomaterials already perform as distributed elements. Thus, TR's two resistors of clay-and-water series and continuous clay are identical to our clay-and-water conduction pattern as we have included the possibility that clays can be continuous in our mixture pattern during our model development.

If the TR model lacks EMT, BHS is completely the opposite. BHS model is

$$\sigma = \sigma_{\text{w}} \phi^m \left(\frac{1 - \sigma_{\text{c}}/\sigma_{\text{w}}}{1 - \sigma_{\text{c}}/\sigma} \right)^m , \tag{8}$$

where ϕ and m are the porosity and the cementation exponent entering the Archie's law, respectively. Mathematically, both BHS and our models have the same parameter numbers (i.e., ϕ, m, and σ_{c} for BHS and F, ξ and σ_{c} for ours), so neither has redundance. That said, it has been emphasized that the BHS model is an implicit function with σ on both sides. The fractional exponent makes BHS can only be solved with complicated numerical methods (e.g., Glover 2010; Niu et al., 2016) or converted to an analytical approximation in the special case of $m = 2$ (e.g., Revil et al., 2019), which restricts its wide usage. Physically, BHS is derived fully via DEM (an EMT method). Since regular geometry is postulated through its DEM derivation (Sen et al., 1981), we argue that BHS's ϕ and m, to some extent, could deviate from the well-received Archie's law since simulations show many factors can influence m (Niu & Zhang, 2018). By contrast, we circumvent this complexity by sorting out the two parallel paths of centered pore fluid and clay-and-water pattern and only use EMT for the second. This is very beneficial as we make our model an easy-to-use explicit function with the legacy of Archie's law.

It shall be underlined that both TR and BHS initially considered clays as conductive solids without EDL variation (c.f., Bussian 1983), it is their further work rather than themselves that involves EDL theories, amongst which, Sauer et al. (1955) and Niu et al. (2016) also discovered that the EDL variation happens merely at relatively extremely low salinities (e.g., < 0.05 S/m), which can be seen as another validation of our non-linear model and its theoretical basis. Furthermore, to make our model solid and convincing, detailed comparisons with TR, BHS, and 10 additional models listed in Glover (2015) are included in the Supporting Information S1, S2, and S3, respectively.

5 Conclusions

We develop a model to characterize the intrinsic non-linear electrical conductivity of clayey rocks and soils. The concave non-linearity is ascribed to the EDL variations and the clay-and-water conduction pattern. The former affects merely at extremely low salinity, while the latter dominates through the whole non-linear portion, whose contributions are included in our model via the averaging scheme and EMT method, respectively. Our model complies with electrochemical theories, coincides with measurements, and is also very easy-to-use. Neglecting the non-linear characteristics of clayey rock and soil conductivity not only leads to erroneous

petrophysical assessment, but also loses potentially invaluable information. We expect this new non-linear formulation could improve the modeling and interpretation of electrical and electromagnetic data in critical zone studies extensively involving freshwater, and pave the way for more quantitative geophysical investigations.

Acknowledgments

Open Research

Data used in this manuscript are from previously published sources that are available through Wyllie & Southwick ([1954](#)), Waxman & Smits ([1968](#)), Friedman ([2005](#)), Lévy et al. ([2018](#)), and Revil et al. ([2019](#)).

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