Characterization of Dielectric Properties of Earth Materials at Low Frequencies

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CHARACTERIZATION OF DIELECTRIC PROPERTIES
OF EARTH MATERIALS AT LOW FREQUENCIES

by

Tarrah Dawn Henrie

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of
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Tarrah Henrie

Introduction

Sharma and de Lima (1992) have proposed a model based on Fixman's theoretical development of charged macromolecules in external fields (1980). There are three types of charges considered: the fixed surface charges that are covalently bonded, the layer of bound counterions, and the diffuse layer (Fixman, 1980, Lyklema, 1983). Figure (1) shows these different layers. Other common theories, such as Schurr’s only consider the bound counterions and the diffuse layer. Schurr assumes that the diffuse layer ions can exchange with the electrolyte. A consequence of this assumption is the lack of polarization of the diffuse layer. This leads to an over estimation of the conductivity and permittivity of clay suspensions (Lima 1992). Fixman’s model allows polarization of the diffuse layer, shown in figure (2). Fixman’s model is different from other models because it accounts for the motion of the ions tangentially and radially in the diffuse layer around a macromolecule. Other models neglect this tangential motion (Lima, 1992).

The model and relevant equations

Fixman’s theory uses the Boltzmann equation in its derivation (1980). The Boltzmann distribution assumes particle independence, this means that there are no significant intermolecular forces at work, so the system must be ideal (Atkins, 1994). For a solution to act ideally the concentration of monovalent ions must be below $1 \times 10^{-3}$ mol/L or if the solution contains bivalent ions the concentration must be below $1 \times 10^{-2}$ mol/L. An additional assumption made by Fixman is that the macromolecule is a sphere. Although this is not true for clay, the model works reasonably well. The dielectric properties of bentonite, or sodium montmorillonite, have been
measured to for a comparison to the model.

The Sharma and de Lima model operates under the premiss that the dielectric properties of a clay suspension can be approximated by a mixing model of the electrolyte and the clay particles. The mixing model must also account for the clay fraction, \( p \). Clay interacts very strongly with the electrolyte because of its inherent negative charge. This means that the dielectric properties of the suspension are not a simple combination of the dielectric properties of the electrolyte and the particles, which is why the model is complicated and non-intuitive.

The total current conductivity of a clay suspension, \( \sigma_o \) is predicted by equation (1). The variables are explained in equations (2) through (6).

\[
\sigma_o = \sigma_w \left[ \frac{2\sigma_o^* + \sigma_c^* - 2p(\sigma_o^* - \sigma_c^*)}{2\sigma_o^* + \sigma_c^* + p(\sigma_o^* - \sigma_c^*)} \right]
\]  

The total current conductivity of the suspension (\( \sigma_o^* \)) is a function of the effective conductivity (\( \sigma_{o,ef} \)) and the effective permittivity (\( \varepsilon_{o,ef} \)) of the suspension. The effective parameters are defined as \( \sigma_{o,ef} = \sigma' + \varepsilon'' \omega \) and \( \varepsilon_{o,ef} = \varepsilon' - \sigma''/\omega \) where \( \sigma' \) and \( \sigma'' \) are the real and imaginary parts of the conductivity of the suspension and \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of the permittivity of the suspension and \( \omega \) is \( 2\pi \) frequency.

\[
\sigma_o^* = \sigma_{o,ef} - i\omega\varepsilon_{o,ef}
\]  

The total current conductivity of the electrolyte (\( \sigma_w^* \)) is a function of the real part of the conductivity (\( \sigma_w \)) and the real part of the permittivity (\( \varepsilon_w \)) of the electrolyte.

\[
\sigma_w^* = \sigma_w - i\omega\varepsilon_w
\]  

The total current conductivity of the particle (\( \sigma_c^* \)) is a function of the real part of the effective conductivity (\( \sigma_{c,ef} \)) and the effective permittivity (\( \varepsilon_{c,ef} \)) of the particle. The effective parameters are modeled by equations (5) and (6).

\[
\sigma_c^* = \sigma_{c,ef} - i\omega\varepsilon_{c,ef}
\]  

The dielectric properties of particles are not measured they are modeled. Equations (5) and (6) are the effective properties of the particle using Fixman's results for a macromolecule in a dilute monovalent electrolyte. Equations (7) through (9) give definitions of parameters used in the
effective properties equations.

\[
\sigma_{\text{c,eff}} = \frac{\delta_1 (1 + \delta_1 A) \sigma_\text{w} - \omega \delta_1^2 B \varepsilon_\text{w}}{(1 + \delta_1 A)^2 + \delta_1^2 B^2}
\]

(5)

\[
\varepsilon_{\text{c,eff}} = \frac{\delta_1 (1 + \delta_1 A) \varepsilon_\text{w} + \frac{\delta_1^2 B \sigma_\text{w}}{\omega}}{(1 + \delta_1 A)^2 + \delta_1^2 B^2}
\]

(6)

where \( A \) and \( B \) are defined in terms of \( y \), where \( y = (\tau \omega)^{1/2} \), and \( \tau \), the relaxation time, is the time required to build a stationary ionic distribution in the bound counterion layer.

\[
A = \frac{(1 - y^3)}{2(1 - y^4)}
\]

(7)

\[
B = \frac{y^2 (1 - y)}{2(1 - y^4)}
\]

(8)

\( \delta_1 \) is defined in equation (9), where \( \beta_1 \) is the surface counterion density necessary to balance the immobile charges on the particle, \( a \) is the particle radius and \( C_1 \) is the cationic concentration in the electrolyte. The value that was used is in table 1.

\[
\delta_1 = \frac{\beta_1}{aC_1}
\]

(9)

For the units to be consistent the real and imaginary part of the permittivity must be absolute as opposed to relative. The permittivity is termed relative if it is divided by the permittivity of a vacuum. Conductivity must be in siemens per meter.

If the real part of the conductivity of the suspension is approximated with \( \varepsilon'' \omega \) then the effective parameters are nonsensical. The effective conductivity becomes \( 4\pi \varepsilon'' \) and the effective permittivity becomes zero. Alternatively, the conductivity of the suspension was obtained using a conductivity meter. The imaginary part of the conductivity can be solved by taking advantage of the loss tangent definition (Lockner, 1985).
There are still several unknown variables: \( C_i, a, \beta_i, \) and \( \tau \). Most of these parameters can be approximated from relationships found in Lockhart, 1980. The relaxation time \( \tau \) is related to the diffusion coefficient \( D \) and the frequency of maximum dielectric loss \( f_{\text{max}} \). The frequency of maximum dielectric loss can be related to the ionic mobility \( u \) and the radius of the particle \( a \) using the Einstein equation where \( F \) is Faraday's constant (Atkins, 1994).

\[
D = \frac{uRT}{F}
\]

(11)

The relaxation time, \( \tau \) can be approximated by equation (12). This relationship for \( \tau \) is predicted by theory (Lockhart 1980, Schwarz 1962).

\[
\tau = \frac{a^2}{2D}
\]

(12)

Equation (13) shows the relationship between the frequency of maximum dielectric loss and the relaxation time.

\[
\tau = \frac{1}{2\pi f_{\text{max}}}
\]

(13)

Using the Einstein relation for \( D \) and inserting it into equation (12) gives a relationship between \( \tau \) and \( u \). Setting this equal to \( \tau \) in equation (13) and solving for \( f_{\text{max}} \) gives:

\[
f_{\text{max}} = \frac{uRT}{\pi a^2 F}
\]

(14)

The value that we used for \( f_{\text{max}} \) was approximated by finding the maximum slope of the real part of the permittivity versus frequency. After calculating \( f_{\text{max}} \), \( a \) and \( \tau \) can be solved for if a typical value is assumed for \( u \). This method was used by Lockhart (1980) as well.

The surface counterion density necessary to balance the immobile charges on the clay (\( \beta_i \)) was taken from Lockhart's value for montmorillonite suspensions, although this value may not be accurate because he used Schwarz's model to calculate it (1980). Sharma and de Lima 1992 also used values taken from other papers. One way to measure the charge density is electrophoresis.
The concentration of cations in the electrolyte can be calculated from the conductivity using another Einstein relation $\sigma_w = uC_1e_0$, where $e_0$ is the electronic charge and $u$ is the cationic mobility.

Table 1

<table>
<thead>
<tr>
<th>Model parameters</th>
<th>1.25 g of clay</th>
<th>5 g of clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity of electrolyte (S/m)</td>
<td>0.0285</td>
<td>0.096</td>
</tr>
<tr>
<td>Conductivity of suspension (S/m)</td>
<td>0.001</td>
<td>0.009</td>
</tr>
<tr>
<td>$\delta_1$</td>
<td>$1.28 \times 10^{24}$</td>
<td>$1.28 \times 10^{23}$</td>
</tr>
</tbody>
</table>

Equipment and methods

The HP 4194A Impedance/gain phase analyzer in conjunction with the HP liquid test fixture were used to take measurements of dilute clay suspensions. Bentonite (sodium montmorillonite) was mixed with distilled water at three concentrations: 1.25 g. bentonite to 100 g. water, 2.5 g. bentonite to 100 g. water, and 5 g. bentonite to 100 g. water. The parallel equivalent capacitance ($C_p$) and the parallel equivalent resistance ($R_p$) of the suspensions were measured because these parameters can be easily related to the real and imaginary part of the dielectric constant.

The relative real part of the dielectric constant ($\varepsilon'_R$) is a function of the gap between electrodes $t$, the parallel equivalent capacitance $C_p$, the area of the plates $A$. The permittivity of free space, $\varepsilon_0$, is what makes the dielectric constant relative instead of absolute. The permittivity of free space is $8.854 \times 10^{-12}$ F/m.

$$\varepsilon'_R = \frac{t \times C_p}{A \times \varepsilon_0}$$  \hspace{1cm} (15)

The relative imaginary part of the dielectric constant is only slightly different from the real part. It is dependent on $R_p$ instead of $C_p$ and divided by a factor of $\omega$.

$$\varepsilon''_R = \frac{t}{\omega \times R_p \times A \times \varepsilon_0}$$  \hspace{1cm} (16)

A simplifying approximation includes the measured air capacitance, $C_0$, which acts as a correction for the gap between the electrodes, the area of the plates, and small environmental variations.
Solving for $C_0$ in equation (17) and substituting it into equations (15) and also putting $\varepsilon_0$ into equation (15) gives the following very simple equations.

$$\varepsilon_0 \approx \frac{I \times C_0}{A} \quad (17)$$

$$\varepsilon'_R = \frac{C_p}{C_0} \quad (18)$$

$$\varepsilon''_R = \frac{1}{R_p \times \omega \times C_0} \quad (19)$$

**Results and Discussion**

The measurements of the permittivity of the bentonite suspensions seem to be accurate. The measured values corresponded reasonably well to values found in literature for similar concentrations (Raythatha, 1986). Figure 3 shows the real and imaginary part of the permittivity for two different clay concentrations. Figure 3 (a) and (b) shows the real part of the permittivity approaching 80 as the frequency becomes higher. This is the expected value for distilled water. The clay particle contribution becomes less important and the water contribution becomes more important at higher frequencies. This same phenomenon can be seen in the imaginary part of the permittivity. As the frequency is raised the imaginary component approaches 0 which is the value expected for distilled water.

The model of the effective conductivity and effective permittivity are shown in figure 4 along with the measured effective parameters. The fit is good, but Sharma and de Lima (1992) had closer fits in their paper. Part of the reason may be that the bentonite was not washed so the ions in solution are salts that were on the clay. This almost guarantees that there are bivalent ions in the suspension. The higher concentration of bivalent ions in the suspension with more bentonite might be the reason that the fit is not as good as the fit for the lower concentration. The clay fraction may also be slightly variable because of particle settling, and layering, which means that the $p$ value used in equation (1) could vary form measurement to measurement. For the suspension with a clay fraction of 0.0125 the conductivity of the suspension and electrolyte were measured as 0.001 S/m, and 0.0285 S/m, respectively. For the suspension with a clay fraction of 0.05 the conductivity of the suspension and electrolyte were measured as 0.009 S/m, and 0.096 S/m, respectively. These values are given in table 1.
Figure 3. (a) The real part of the dielectric permittivity for a bentonite suspension of 1.25 g. of clay and 100 g. of distilled water. (b) The real part of the dielectric permittivity for a bentonite suspension of 5.00 g. of clay and 100 g. of distilled water. (c) The imaginary part of the dielectric permittivity for a bentonite suspension of 1.25 g. of clay and 100 g. of distilled water. (d) The imaginary part of the dielectric permittivity for a bentonite suspension of 5.00 g. of clay and 100 g. of distilled water.
Figure 4. (a) The modeled and calculated effective permittivity for a bentonite suspension of 1.25 g. of clay and 100 g. of distilled water. (b) The modeled and calculated effective conductivity for a bentonite suspension of 1.25 g. of clay and 100 g. of distilled water. (c) The modeled and calculated effective permittivity for a bentonite suspension of 5.00 g. of clay and 100 g. of distilled water. (d) The modeled and calculated effective conductivity for a bentonite suspension of 5.00 g. of clay and 100 g. of distilled water.
The value of $\delta_1$ is an approximation. The model, however is not very sensitive to this parameter. It has to change several orders of magnitude to change the fit of the curve. If this approximation is anywhere near the real value then this is not a big source of error.

Another source of error may be the HP 4194A. Hewlett Packard was kind enough to loan us this machine to test for a few months. This machine should undergo a performance test every six months, but had not for about a year. This test insures that the machine is operating within its specifications (Hewlett Packard, 1996). A measurement of water showed a relative dielectric constant of 79 as opposed to 81 at 25°C, this deviation may be a reflection of the need for machine testing.

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**Variable table**

- $\overline{\sigma}_o$ = The total current conductivity
- $p$ = Clay fraction
- $\sigma_{ef}$ = The effective conductivity
- $\varepsilon_{ef}$ = The effective permittivity
- $\omega = 2\pi f = $ frequency
- $a$ = The particle radius
- $C_1$ = The cationic concentration in the electrolyte
- $\tau = $ The relaxation time
- $D = $ Diffusion coefficient
- $u = $ Ionic mobility
- $R = $ Gas constant
- $T = $ Temperature
- $F = $ Faradays constant
- $f_{\text{max}} = $ The frequency of maximum dielectric loss
- $e_o = $ Electronic charge
- $\varepsilon_o = $ Permittivity of free space $= 8.854 \times 10^{-12} F/m$
- $t = $ Gap between electrodes
- $C_p = $ Equivalent parallel capacitance
- $R_p = $ Equivalent parallel resistance
- $C_o = $ Air capacitance

Subscripts $o, w, c$ denotes suspension, electrolyte, particle respectively
Subscript $R$ denotes relative
Prime and double prime denote real and imaginary
Literature Cited