Utah State University

From the SelectedWorks of Stephen E. Bialkowski

January 1, 2002

Using an Expectation-Maximization Algorithm to Obtain Dielectric Relaxation Time Spectra of Aqueous Montmorillonite Clay Suspensions

Stephen E. Bialkowski, Utah State University
Lynn Dudley
Dani Or

Available at: https://works.bepress.com/stephen_bialkowski/82/
Using an Expectation–Maximization Algorithm to Obtain Dielectric Relaxation-Time Spectra of Aqueous Montmorillonite Clay Suspensions

STEPHEN E. BIALKOWSKI,* LYNN DUDLEY, and DANI OR
Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300 (S.E.B.); and Department of Plants, Soils, and Biometeorology, Utah State University, Logan, Utah 84322-4820 (L.D., D.O.)

Determination of relaxation-time distributions from dielectric spectra of complex impedance or dielectric permittivity remains a challenge. This problem is one of a wider class of ill-posed inverse problems where the measurement is a superposition or convolution of functions containing the sought-after information. An expectation–maximization (EM) algorithm is shown to be useful for obtaining dielectric relaxation-time distributions from impedance data. This algorithm is stable and converges to realistic relaxation-time spectra without the need for constraints or initial values. The implementation used herein updates expectations in an iterative multiplication step. The models and basic assumptions of impedance spectroscopy are outlined in the first part of this paper. Frequency-dependent impedance measurements are obtained for calibration samples and saturated montmorillonite clays. The EM algorithm is subsequently used to determine the dielectric relaxation times. The dielectric relaxation-time spectra allow facile interpretation of otherwise complicated impedance.

Index Headings: Impedance spectra; Deconvolution; Montmorillonite.

INTRODUCTION

A primary goal in impedance spectra analysis is to obtain information regarding the surface and the state of water surrounding the suspended particles. This information may be in the form of surface or Stern layer conductivity and dielectric permittivity due to water polarization. Although some disagreement exists regarding the motion of ions surrounding the particles, the dielectric relaxation time is nonetheless an important diagnostic for soil constituents. Dielectric relaxation-time information may be used to calculate surface properties such as zeta potential and surface charge. These surface properties may be useful for calculation of ion mobility in saturated and partially saturated soils and vadose zone ion transport.

It is unfortunate that important information regarding ion mobility and surface-water dielectric relaxation is obtained via application of complex models to the measured impedance spectra. This application often involves nonlinear or constrained regression of unknown error surfaces or data construction, via convolution, of frequency-dependent impedance spectra based on relaxation-time distributions. Nonlinear data regression can easily result in physically unrealizable parameters. There are many models that may be applied to analyze the data. It is interesting that application of different models can result in contradictory predictions regarding surface conductivity and dielectric constant. Thus, information regarding surface conductivity and surface water polarizability appears to be hopelessly lost in difficult, if not conflicting, models.

In this work we explore a direct approach to determine surface conductivity and colloid permittivity in aqueous suspensions of sodium and calcium montmorillonite clays. An expectation–maximization (EM) algorithm is used to determine the relative weights of a series of Debye dielectric relaxation functions from the frequency-dependent impedance spectra. This normally ill-posed deconvolution proceeds directly and monotonically to the solution. The resulting weights, or amplitudes, are the relaxation-time spectra of the sample. The EM algorithm used implicitly constrains the range of possible outcomes to have physically realizable, positive-only amplitudes. The latter is due to the use of a Poisson probability distribution to describe the random “shot noise” in the electrical current measurements. Although least-squares like Macdonald’s LEVM program may work well in cases where specific model parameters are sought, we herein describe a general deconvolution that is independent of model or assumed number of relaxation times that is based on the correct noise statistics. Dielectric characteristics of samples are obtained using the Maxwell–Wagner model for suspensions. Justification for linear combinations of Debye dielectric relaxation functions is found through the circuit equivalent of the Maxwell–Wagner complex conductance shown by Bonanos and Lilley.

In this paper, both synthetic and experimental impedance data of glass and clay suspensions are obtained from 100 Hz to 15 MHz. The data are used to calculate complex impedance and are subsequently converted to modulus. The imaginary part of the complex modulus is then represented as a series of Debye dielectric functions. The imaginary modulus is chosen because it reduces the influence of the Warburg diffusion while emphasizing conductivity and dielectric properties of the suspended particles. The imaginary modulus is equivalent to the imaginary impedance for single relaxation-time dielectrics. The algorithm is found to converge to seemingly correct relaxation-time spectra even with incomplete or noisy data.

THEORY

Impedance spectroscopy is a technique used to characterize materials by their complex conductivities and/or dielectric properties. Impedance measurements are often performed by applying a low-voltage, ac potential to a
Bonanos and Lilley give the relationship between the Maxwell–Wagner effective medium model and the Voigt equivalent circuit elements, as shown in Eqs. 5 and 6. In these equations, $Z(\omega)$ is the complex impedance, with real, $Z'(\omega)$, and imaginary, $Z''(\omega)$, components.

$$Z(\omega) = Z'(\omega) + iZ''(\omega)$$  

(2)

In electrical circuits, the real part is resistance while the imaginary part is due to capacitance and inductance reactance. In materials, the real part may be due to ion conductivity while the imaginary part is due to ion or solid polarizability. In general, the real resistance and imaginary reactance are functions of frequency. Electrical current measurements are thought to be shot-noise-limited in terms of the noise probability density.

The aqueous suspensions of small-diameter solids are two-component systems that produce complex impedance behavior. This behavior can be interpreted through equations resulting from the Maxwell–Wagner model.15 The Maxwell–Wagner model calculates a complex conductivity for two-component systems replacing a homogeneous medium with the same impedance characteristics. Details of this model are discussed in Macdonald’s book.11,12 The complex conductivity is given as:

$$\psi = \sigma + i\omega \varepsilon$$  

(3)

where $\sigma$ is the real component of the conductivity, $\varepsilon$ is the dielectric coefficient, and $\omega$ is the angular frequency. For a volume fraction, $x_2$ of phase 2, the Maxwell–Wagner impedance is:

$$\psi_i = \frac{2\psi_1 + \psi_2 - 2x_2(\psi_1 - \psi_2)}{2\psi_1 + \psi_2 + x_2(\psi_1 - \psi_2)}$$  

(4)

$\psi_1$ and $\psi_2$ are the complex impedance of the two phases and $\psi_i$ is the total impedance. It is difficult for us to visualize the complex impedance and how changes, even in volume fraction, affect the relaxation times and magnitude of the phase-two contributions.

The in-phase and quadrature impedance components may also be understood in terms of Voigt equivalent circuit elements, made up of a parallel capacitor and resistor, complex conductivity, or equivalently complex dielectric constants. All three are related to the Maxwell series layer model:12

$$G_1 = \frac{\sigma_1 A_\infty - \varepsilon_1 A_\sigma}{\sigma_1 B_\infty - \varepsilon_1 B_\sigma}, \quad G_2 = \frac{\sigma_2 A_\infty - \varepsilon_2 A_\sigma}{A_\infty B_\infty - B_\sigma A_\sigma}.$$  

(5)

$$C_1 = \frac{\sigma_1 A_\infty - \varepsilon_1 A_\sigma}{\sigma_1 B_\infty - \varepsilon_1 B_\sigma}, \quad C_2 = \frac{\sigma_2 A_\infty - \varepsilon_2 A_\sigma}{A_\infty B_\infty - B_\sigma A_\sigma}.$$  

Bonanos and Lilley give the relationship between the Maxwell–Wagner effective medium model and the Voigt equivalent circuit elements, as shown in Eqs. 5 and 6. In these equations, $G_1$ and $G_2$ (Ω⁻¹) are the conductance of the two Voigt circuit resistors and $C_1$ and $C_2$ (F) are the capacitance of the parallel capacitors. The $\sigma_{i,2}$ and $\varepsilon_{i,2}$ are the conductivity and dielectric coefficient of the solvent (subscript 1) and the clay (subscript 2), and $x_2$ is the volume fraction of the clay. These equations may be used to connect measured impedance to the conductivity and dielectric coefficient of the clay.

$$A_a = 2\sigma_1 + \sigma_2 - 2x_2(\sigma_1 - \sigma_2)$$  

$$B_a = 2\sigma_1 + \sigma_2 + x_2(\sigma_1 - \sigma_2)$$  

$$A_s = 2\varepsilon_1 + \varepsilon_2 - 2x_2(\varepsilon_1 - \varepsilon_2)$$  

$$B_s = 2\varepsilon_1 + \varepsilon_2 + x_2(\varepsilon_1 - \varepsilon_2)$$  

(6)

The dielectric coefficient and conductivity of the suspending solution is obtained independently. We assume the dielectric to be simply that of water at the measurement temperature. The conductivity is measured with a dc conductivity meter. The problem thus reduces to one of determining the Voigt equivalent circuit values from ac impedance measurements.

Using the dielectric coefficient of the clay mineral will result in two unknown parameters, namely $\sigma_2$ and $x_2$. Model calculations using Eqs. 5 and 6 over a practical range of experimental conditions show that relaxation times, the $RC$ time constants, expressed here by the ratio $\tau = C/G$, of the Voigt equivalents:

$$\tau_1 = \frac{\varepsilon_1}{\sigma_1}, \quad \tau_2 = \frac{2\varepsilon_1 + \varepsilon_2 - 2x_2(\varepsilon_1 - \varepsilon_2)}{2\sigma_1 + \sigma_2 - 2x_2(\sigma_1 - \sigma_2)}$$  

(7)

are not affected by volume fraction ($x_2$) over the practical range of values. The analysis of the surface conduction of clay suspensions may thus be reduced to determination of dielectric relaxation times from the ac impedance data.

The Maxwell–Wagner model thus predicts two dielectric relaxation times, one due to the liquid solvent, with unavoidable electrolytes, and the second due to the polarization of the suspended particles, surrounded by the aqueous electrolyte solution. The first relaxation time is a function only of the properties of the aqueous solution that the particles are suspended in, while the second relaxation time, sometimes referred to as the Maxwell–Wagner relaxation time, is a function of the conductivity and dielectric constant of both solvent and particle.

The two-relaxation-time model assumes that the clay colloids are spherical. Fricke17 showed that spheroid particles might exhibit up to three different relaxation times. Solutions of asymmetrical particles will thus have four relaxation times.12 It is likely that heterogeneous clay suspensions will exhibit relaxation-time distributions, rather than the simple two Voigt equivalent circuit relaxation.
To obtain a relaxation-time distribution, we first consider the sample to be composed of a collection of circuit elements, as in the Fricke model. These elements each have a characteristic relaxation time, $\tau$. In this case the sample impedance is:

$$Z(\omega) = \int_0^\infty A(\tau) \left( \frac{i\omega \tau}{1 + i\omega \tau} \right) \, d\tau$$

(8)

$A(\tau)$ is the amplitude of the element with relaxation time, $\tau$. The element may be thought of as a Voigt equivalent parallel resistor and capacitor with time constant $RC$, or part of a physical relaxation process, e.g., due to motion of charge carriers. A discrete form of Eq. 8 where only the imaginary part of the impedance or modulus is used in practice is:

$$Z''(\omega) = \sum_{\tau = \tau_{\text{min}}}^{\tau_{\text{max}}} A(\tau) \left( \frac{\omega^2 \tau_j^2}{1 + \omega^2 \tau_j^2} \right)$$

(9)

The sum is over the range of practical relaxation times. This is typically from 1 ps to 1 s in a scale that is linear in the logarithm of time. The measured impedance, $Z(\omega)$, is thus modeled as a series of dielectric dispersion functions, each with a relaxation time of $\tau$ and with an amplitude of $A(\tau)$. We call the relaxation-time-dependent amplitude distribution the “relaxation-time spectrum” of the sample.

An expectation–maximization algorithm based on maximum likelihood estimation of Poisson or shot-noise-limited processes is used to determine the $\hat{A}(\tau)$. The algorithm is:

(1) Calculate the expectation $\hat{Z}(\omega)$ using Eq. 7 with the most recent relaxation-time spectrum, $A(\tau)$.
(2) Maximize the probability that the $A(\tau)$ are from the initial distribution with:

$$A_{n+1}(\tau) = A_n(\tau) \sum_{\tau = \tau_{\text{min}}}^{\tau_{\text{max}}} \left( \frac{\omega^2 \tau_j^2}{1 + \omega^2 \tau_j^2} \right) / Z''(\omega)$$

(10)

(3) Update the expectation and test for convergence.
(4) If the convergence criteria have not been met, repeat, starting with step 1.

For initial values, all amplitudes are taken as $A(\tau) = 1$. One property of this algorithm that is particularly appealing is that the amplitudes are always physically realizable. That is, they can only be positive valued. Thus, constrained Laplace inversion is not required, and thus, there is no bias in the resulting amplitude spectrum. The EM algorithm used here has been shown to be more accurate than methods of deconvolution using Tikhonov and least-squares Kalman methods in a study comparing several deconvolution methods.

Step 3 requires a test for convergence. There are several different criteria that may be applied. In this study, the number of iterations was fixed to a value. Error analysis was subsequently performed to determine if there was any bias in the results.

**EXPERIMENTAL**

Two types of samples were used in this study, a control sample of glass beads in deionized distilled water and bentonite clays modified to the sodium or calcium forms. The glass beads were 60 $\mu$m in diameter (Cataphote, Inc). Panther Creek Colorado montmorillonite was obtained from Ward’s. In addition, the algorithm was tested on data synthesized using Eqs. 2–4 with dielectric coefficient and surface conductivity values expected from the clay samples.

The Montana montmorillonite clay was first soaked in three volumes of 1 M NaCl or CaCl$_2$ solutions. The suspensions were initially 10% by volume. The clay was separated by centrifugation, the solvent replaced, and the solid mixed with the fresh solution. After conversion to calcium or sodium forms, the clay was resuspended in water by performing 5 to 10 soaks in 5 volumes of distilled deionized water for several hours followed by centrifugation. The clay was size fractionated by differential centrifugation. The resulting solutions were stored for a maximum of one month. Coagulation was apparent even after 1 week. The dc conductivity was checked with a conventional conductivity meter.

Impedance is measured with a Hewlett Packard model 4189A impedance analyzer A Hewlett Packard model 16452 liquid dielectric test cell using a 0.3-mm electrode gap was used. The sample cell was placed in a circulating water bath for temperature-dependent studies. The frequency range of the instrument using the liquid cell was 100 Hz to 15 MHz. Linear and logarithm scans of impedance were performed on each sample. A PC computer was used to collect the data in digital format using the IEEE-488 (HPIB) interface. The data were subsequently read into an MS Excel spreadsheet for analysis.

The raw data were in the form of real and imaginary dielectric coefficients and parallel resistance, $R_p$, and capacitance, $C_p$, as functions of frequency. The latter were used to calculate the impedance, $Z(\omega)$, and modulus, $M(\omega)$, using:

$$Z'(\omega) = \frac{X'(\omega) R_p}{X'(\omega) + R_p^2}, \quad Z''(\omega) = \frac{X''(\omega) R_p^2}{X''(\omega) + R_p^2}$$

$$X_c(\omega) = \frac{1}{\omega C_p}, \quad M(\omega) = i\omega C_p Z(\omega)$$

(11)

$C_p$ is the empty cell capacitance.

The EM algorithm was applied to $Z''(\omega)$ and $M''(\omega)$ data. Generally, linear and log frequency data were combined prior to calculating the relaxation-time spectra with EM. The deconvolution algorithm was coded in the C++ programming language. The number of iterations as well as the summed squared residuals between the expectation and the impedance of modulus data could be used to terminate the algorithm. The number of data points (times) per decade was an adjustable parameter. The latter was typically 20 points per decade.

**RESULTS**

Numerical simulations of impedance spectra expected from the montmorillonite clay suspensions were performed to test the data analysis procedure. Calculations used values that mimic laboratory measurements. Na$^+$ and Ca$^{2+}$ montmorillonite suspensions exhibit conductance on the order of about 1 mS/m. The clay, having a net negative charge, will serve as an exchange site with
cations in solution. For modeling purposes, the surface conductivity, and thus the conductivity of the clay, was assumed to be about ten times that of the bulk water. Similar conductivity ratios have been observed in surface-modified polystyrene samples. The dielectric constants for water, $7.44 \times 10^{-10}$ F/m, and silica, $3.54 \times 10^{-11}$ F/m, are used. The Warburg diffusion impedance term is modeled as $A\omega^{-1/2}$. The value of the multiplier, $A$, was chosen to approximate experimental measurements. Using 1 mS/m for the water and 10 mS/m for the clay conductivity, and a clay volume fraction of 10%, results in relaxation times for water of 742 ns and a Maxwell–Wagner relaxation time of 100 ns. The resulting frequency-dependent impedance is illustrated in Fig. 2.

The impedance is shown two different ways. First, the real and imaginary components of the frequency-dependent impedance are plotted as functions of log frequency. The Warburg diffusion impedance component is that downward sloping signal most apparent at and below 10,000 rad/s. The imaginary component of the impedance exhibits a peak at the water-resonance frequency. This peak is slightly broadened to the high-frequency side due to the Maxwell–Wagner component. However, it is not apparent that there is a second relaxation component to the impedance at the 10% volume fraction.

The second plot in Fig. 2 shows the impedance-plane plot of imaginary vs. real impedance components. The frequency is labeled at the decade points showing the development of the arc with frequency. Though not immediately apparent, the arc is not a perfect semi-circle and exhibits distortion at higher frequencies, which are plotted in the lower impedance regions of the impedance-plane plot. This slight distortion is due to the Maxwell–Wagner relaxation. The line extending to the upper right, made up of impedance below 5 kHz, is the Warburg diffusion impedance. Figure 3 shows the data after it is processed to yield the modulus. The modulus is a unitless quantity. The inverse is equal to the dielectric permittivity. Plotting the modulus clearly shows the effect of the Maxwell–Wagner relaxation in both the frequency-dependent modulus and impedance-plane plots shown in Figs. 3A and 3B. In fact, analysis of the modulus data plots may alone be used to deduce the relaxation-time constants if the number of relaxation times is known ahead of time.

The imaginary part of the modulus is used to find the relaxation-time distribution through the use of the EM algorithm. Figure 4 shows the relaxation-time distribution found from the $M''$ data similar to that illustrated in Fig. 3. The theoretical relaxation times for this simulation were 742 and 87 ns. These are the relaxation times expected for a 16% (v/v) clay suspension in aqueous solution with 1 mS conductivity of the aqueous phase. The surface conductivity was 10 mS.

The relaxation-time distributions obtained for synthetic data were found to faithfully estimate the original model times. The relaxation-time distribution width does decrease with the number of iterations, up to a point. After this, occurring at about 50,000 iterations, there was no
improvement in the precision of the fit. Nonetheless, subsequent calculations used 100,000 iterations. It was also observed that the precision did not depend on the resolution of the $A(\tau)$ array. Calculations obtained using 10, 20, 40, and 80 points per decade of relaxation time all produced the same relaxation-time spectrum. On the other hand, the range of the relaxation-time spectrum had considerable influence on the width of relaxation-time distributions calculated for the impedance and modulus with two single (i.e., not broadened) relaxation times. Smaller, lower relaxation-time limits produced narrower distributions. In addition, the relaxation-time spectra exhibited a broad distribution from the Warburg diffusion term and when the minimum relaxation time was too long. The Warburg diffusion term is a $\omega^{-1/2}$ frequency-dependent term apparent at lower frequencies. A flat broad relaxation-time feature occurred at longer relaxation times in this case. The influence of Warburg diffusion on the relaxation-time spectra was reduced using the modulus. This is owing to the weighting of higher frequencies in the modulus calculation.

Shown in Fig. 5 are data for 10% (v/v) calcium montmorillonite clay obtained at 55 °C. The primary relaxation corresponds to the solvent water. The two relaxation times are at 100 and 10 ns. The longer relaxation time indicates an aqueous-phase conductivity of about 6.0 mS. This is obtained from Eq. 7 with $\varepsilon_1 = 6 \times 10^{-10}$ F m$^{-1}$ for water at 55 °C. The secondary peak, shorter relaxation time, is thought to be due to the clay suspension. This being the case, and assuming a dielectric constant of 3.54 $\times 10^{-11}$ F m$^{-1}$, the surface conductivity of the clay is about 90 mS. This is a factor of 15 and is about the factor of 10 predicted based on other measurements. The relative magnitude of the second relaxation peak, as well as the clay conductivity being about an order of magnitude greater than that of the aqueous phase, is also consistent with the 10% (v/v) samples.

**DISCUSSION**

The procedure was tested in terms of the ability to find realistic relaxation-time spectra under a number of different conditions. We find that convergence acceleration by initial “guesses” should generally not be attempted. In fact, this acceleration often results in slower convergence. This is presumably due to the fact that it is more difficult to pass out of the local minimum in the expectation. A number of different relaxation-time distribution models are tested. The algorithm is stable and exhibits satisfactory performance in all cases tested. The main drawback to the algorithm is the slow convergence.

**ACKNOWLEDGMENTS**

We wish to thank the undergraduate students who helped obtain and analyze these data, Chad Junkermeier, Heather Ellsworth, Eric Payton, Sara Johnson, and Laura Jae Bracken, and the USDA for financial support of this project.