

Rock/water interaction in dielectric properties: Experiments with hydrophobic sandstones

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ABSTRACT

The dielectric constant of a partially saturated sandstone varies as a function of the level of water saturation. Experimental data indicate that rock/water interaction, at low saturations, has a large effect on the measured dielectric response. To theoretically predict the dielectric constant of the rock/water/air system, this rock/water interaction must be accounted for by including the effect of the water wetting the rock solid. Alternatively, if the rock/water interaction can be eliminated, a three-component (dry rock, water, and air) mixing law can be used to model the dielectric behavior. In this laboratory study, a chemical treatment is used to change four water-wet sandstones into hydrophobic sandstones. In three hydrophobic samples the rock/water interaction, seen in the data for the water-wet samples, is eliminated and the dielectric constant of the partially saturated sandstones can be simply modeled as a dry rock/water/air system. This experimental study illustrates the importance of the chemical state of the rock surfaces in determining the dielectric behavior of sandstones.

INTRODUCTION

The dielectric response of any multicomponent system will depend upon the volume fraction and dielectric constant of each individual component. The development of a method to theoretically predict the dielectric behavior of multicomponent systems, given such information about the individual components, has been a topic of research for a number of years in many fields of study. Of interest in this paper is the dielectric response of partially saturated sandstones. This geological material is an example of a multicomponent

system, a rock/water/air system, with a dielectric response dependent upon the nature of the individual components.

It is generally assumed in theoretical modeling of dielectric properties that the dielectric responses of the individual components do not change when the components are combined to form the total system, i.e., there is no interaction between the components. In this respect, the rock/water/air system is unique. Unlike other systems for which a theoretical treatment has been developed, two of the components, the rock and the water, do interact, strongly, to affect the dielectric behavior of the mixture. The specific nature of the rock/water interaction is not yet well understood, and will depend upon the composition of the solid surface. As reviewed by Parks (1990), the surfaces of many minerals will hydroxylate and hydrate in the presence of water, leading to the development of a region of distinct chemical and physical properties. The focus of this study is the fact that the wetting of the rock solid by the water, and the resulting rock/water interaction, introduces a significant effect that must be accounted for in modeling the dielectric response of porous rocks.

The effect of rock/water interaction on the dielectric behavior of saturated sandstones has been shown in studies by Knight and Nur (1987) and Knight and Endres (1990). In these studies the real part of the dielectric constant K' of sandstone samples was measured as the level of water saturation S_w was varied; S_w is the volume fraction of the pore space filled with water, the remainder being filled with air. The frequency of the measurements was 60 kHz to 4 MHz. Figure 1 shows the form of the measured data schematically. In all cases, there is a dramatic increase in the dielectric constant of the sandstone with the addition of a small amount of water in the region $0 < S_w < S_w^0$; where S_w^0 has been defined as the critical saturation point (Knight and Nur, 1987). Such an increase at low saturations was attributed to interactions between the solid rock and a surface

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layer of water 1 nm in thickness wetting the solid surface (Knight and Endres, 1990).

Using the complex refractive index method CRIM (Wharton et al., 1980) and the three-component effective medium theory of Feng and Sen (1985), it was shown by Knight and Endres (1990) that K' of a sandstone at various levels of water saturation can be predicted. However, if the three components are defined as the dry rock, the water, and the air, the predicted K' underestimates the measured K' ; this is shown schematically in Figure 1. The difference between the measured and predicted values is clearly a result of the effect at low saturations. When the system is redefined as being composed of wetted rock, water, and air, we can accurately model the data in the region $S_w^0 < S_w < 1$, with the dielectric constant of the wetted rock being determined from the dielectric constant measured at S_w^0 .

The rock/water interaction is an additional factor in the dielectric response of rock/water systems that is not accounted for in theories that predict the dielectric constant of a rock at various levels of saturation from the properties and volume fractions of the dry rock, water, and air. The approach taken by Knight and Endres (1990) is to define wetted parameters that include the interaction and to use existing theories to model the data in the region $S_w^0 < S_w < 1$. In this study, we now address the problem of rock/water interaction in an experimental way. We define the components as dry rock, water, air, and chemically treat the solid to eliminate the surface interaction with the water, i.e., we

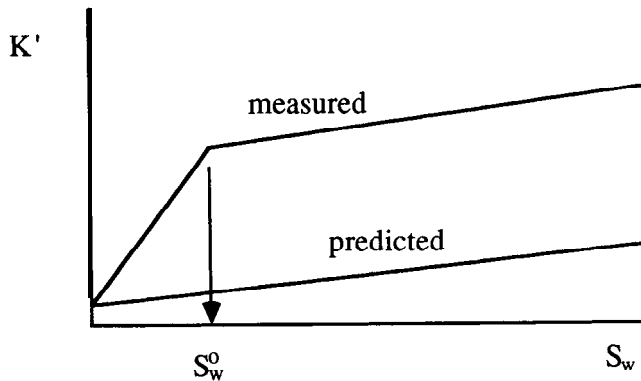


FIG. 1. Schematic illustration of the variation in the dielectric constant (K') of a sandstone as a function of the level of water saturation (S_w). The theoretically predicted and measured dielectric data are compared.

create hydrophobic sandstones. As can be seen in our experimental results, the data can then be modeled as a dry rock/water/air system using CRIM. We restrict ourselves to the modeling of data collected at 1 MHz, as at lower frequencies additional effects associated with pore-scale fluid distribution and the conductivity of the system become dominant; these effects cannot be accounted for in modeling with CRIM. The saturation effect at low saturations is eliminated in the hydrophobic sandstones, confirming the significant role of rock/water interaction in determining the dielectric response of water-saturated sandstones.

SAMPLE DESCRIPTION AND EXPERIMENTAL PROCEDURE

The four samples used in this study, Beaver, Indiana Light, Berea, and Delaware Brownstone, are all quarried sandstones. The petrographic descriptions are given in Table 1 and were taken from the Stanford Rock Physics Catalog. Also included in Table 1 is the porosity ϕ of each sample, measured using a helium porosimeter. Laboratory measurements were made on thin disk-shaped samples, approximately 5 cm in diameter and 0.5 cm thick. A two-electrode technique was used with electrodes applied by sputtering 50 to 100 nm of gold or platinum on the two opposite faces of the sample disks. Data were collected at a frequency of 1 MHz using a Hewlett-Packard impedance analyzer. The measured parameter is the complex admittance Y^* of the sample

$$Y^* = G_p + i\omega C_p, \quad (1)$$

where G_p is the parallel conductance, C_p is the parallel capacitance, and ω is angular frequency. The complex relative dielectric permittivity K^* can be written as $K^* = K' - iK''$. The real and imaginary parts of K^* are related to the measured parameters as follows:

$$K' = \frac{C_p t}{\epsilon_0 A}, \quad (2)$$

$$K'' = \frac{G_p t}{\omega \epsilon_0 A}, \quad (3)$$

where A is the cross-sectional area of the sample, t is its thickness, ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.85 \times 10^{-12}$ F/m), and ω is angular frequency. The parameters K' and K'' defined in this way are referred to as effective parameters, as they are what is actually measured in collecting complex admittance data. Further details of the measure-

Table 1. Petrographic descriptions and porosity measurements for the samples.

Sample	Framework Grains (% of solid)							Cement/Matrix (% of solid)				Porosity
	Qtz	Ch	Fsp	Carb	Lith	Opq	O	Qtz-O	Clay	Carb	Opq	
Beaver	82	—	tr	—	1	—	—	17	tr	—	—	0.084
Indiana Light	67	3	12	—	1	1	4	—	12	—	—	0.257
Berea	58	2	3	—	9	tr	tr	12	8	8	—	0.195
Delaware Brownstone	80	4	—	—	2	—	—	3	1	—	10	0.128

Qtz-quartz, Ch-chert, Fsp-feldspar, Carb—carbonate, Lith-lithics, Opq-opaques, O-other, Qtz-O-quartz overgrowths, tr-trace.

ment technique, calibration, and sample preparation are given in Knight and Nur (1987).

In the first stage of the laboratory study, a complete set of dielectric measurements were made on the four samples prior to any chemical treatment. Each sample was fully water saturated with degassed, distilled water, then the level of water saturation was decreased through evaporative drying with the weight monitored to determine the saturation level. Dielectric measurements were made at the various levels of water saturation. We were unable to collect data on a fully saturated ($S_w = 1$) sample, as the sample dried in transferring it from the saturating set-up to the sample holder for dielectric measurements.

The next stage of the study involved a chemical treatment of the four samples to change the hydrophilic solid surfaces throughout the rock samples into hydrophobic solid surfaces. Each sample was treated with Quilon-C®, a chromium complex containing a fatty acid group. The chromium in Quilon-C® reacts with negatively charged surfaces such as silica, exposing the fatty acids. The fatty acid groups repel water, thus making the rock surfaces hydrophobic. The specific procedure we used is a modified version of that used by Lewis (1988). A dry sample was placed in a beaker inside a vacuum chamber and first evacuated for two hours. A 20% solution of Quilon-C® in isopropyl alcohol was then poured through a funnel into the evacuated sample chamber. The sample was soaked in the solution for two days then heated in an oven at 60°C for one day. This entire procedure was repeated twice to obtain a complete and stable treatment.

As a means of determining the extent to which each sample had been altered from a hydrophilic to a hydrophobic state, spontaneous imbibition experiments were conducted. To determine how much water a sample spontaneously imbibed, a dry sample was soaked in 200 ml of distilled water for three hours before and after sample treatment with Quilon-C®. The saturation levels reached by each of the samples are summarized in Table 2. In each case, the volume of water imbibed decreased by a significant amount following treatment. There was a 90% reduction in the volume of imbibed water for Beaver, an 89% reduction for Indiana Light, a 93% reduction for Berea, and a 76% reduction for Delaware Brownstone.

With chemical treatment of the sample completed, each sample was again saturated, under pressure with degassed distilled water, and dielectric measurements made as the saturation level decreased through evaporative drying.

Table 2. Spontaneous imbibition data obtained from the samples to determine the success of the chemical treatment.

Sample	S_w before treating sample with Quilon-C®	S_w after treating sample with Quilon-C®
Beaver A	0.39	0.04
Indiana Light (V)	0.66	0.07
Berea 100	0.57	0.04
Delaware Brownstone	0.41	0.10

EXPERIMENTAL RESULTS

The dielectric data collected at a frequency of 1 MHz are presented in Figures 2 to 5 as K' versus S_w . Each figure contains the data for one sample, collected for the untreated sample (plotted as open squares) and the chemically treated samples (plotted as open circles). We will refer to the untreated samples as the water-wet samples, and the treated samples as the hydrophobic samples; although we note that the samples are not fully hydrophobic as there is still some spontaneous imbibition of water.

Figure 2 contains the dielectric data for Beaver Sandstone. The data for the water-wet sample have the same form as has been previously observed in measurements of the dielectric constant of sandstones as a function of saturation (schematically shown in Figure 1). The distinctive region at low saturations ($0 < S_w < S_w^0$) can be clearly seen, within which K' increases dramatically with a small increase in S_w . Above S_w^0 , found for this sample to be at approximately

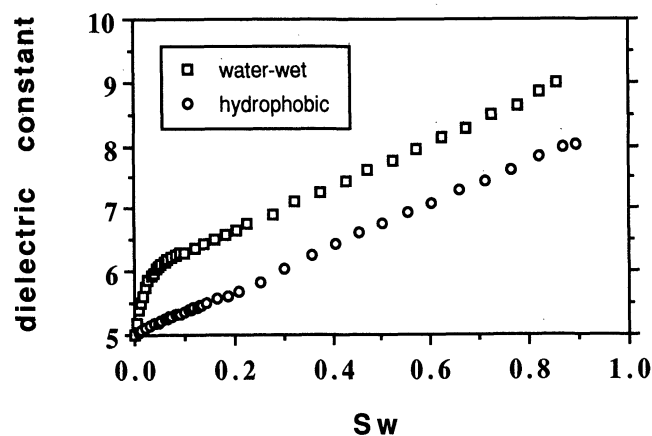


FIG. 2. Dielectric constant of Beaver Sandstone versus the level of water saturation S_w . Data were collected on the original water-wet sample and after chemical treatment was applied to make the sample hydrophobic.

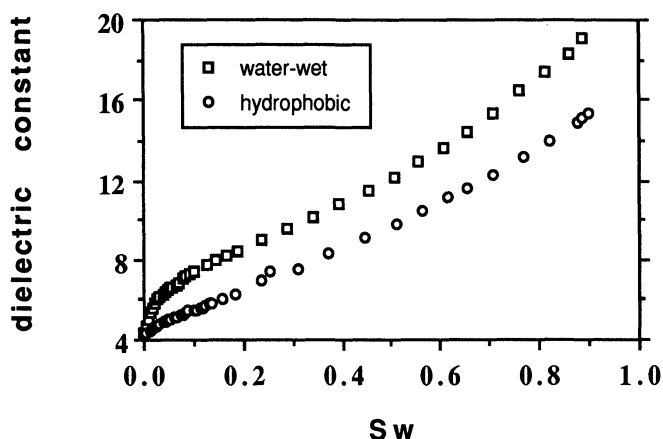


FIG. 3. Dielectric constant of Indiana Light Sandstone versus the level of water saturation S_w . Data were collected on the original water-wet sample and after chemical treatment was applied to make the sample hydrophobic.

$S_w = 0.07$, the data follow a linear trend of much reduced slope with K' increasing with S_w .

It was previously suggested (Knight and Endres, 1990) that the form of the data in the region $0 < S_w < S_w^0$ is a result of the rock/water interaction. The results from the hydrophobic sample strongly support this idea; the increase in the measured dielectric constant in the low saturation region has been eliminated. The hydrophobic nature of the solid surface prevents the rock/water interaction from occurring, and thus eliminates the corresponding dielectric constant increase at low saturations. Instead of two distinct regions in the dielectric data, there is one linear region of constant slope. It is important to note that the data for the treated sample approximately parallels the untreated data in the region $S_w^0 < S_w < 1.0$.

In Figure 3 are the data for Indiana Light. Again we see two regions in the data for the water-wet sample with S_w^0 approximately equal to 0.08. In the data for the hydrophobic sample, the lower saturation region has been eliminated, and

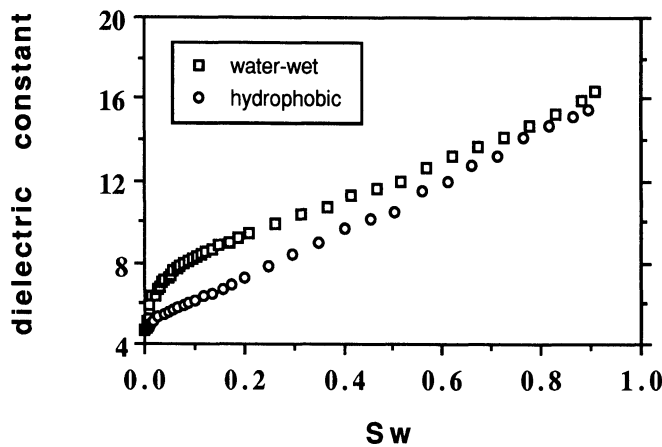


FIG. 4. Dielectric constant of Berea Sandstone versus the level of water saturation S_w . Data were collected on the original water-wet sample; and after chemical treatment was applied to make the sample hydrophobic.

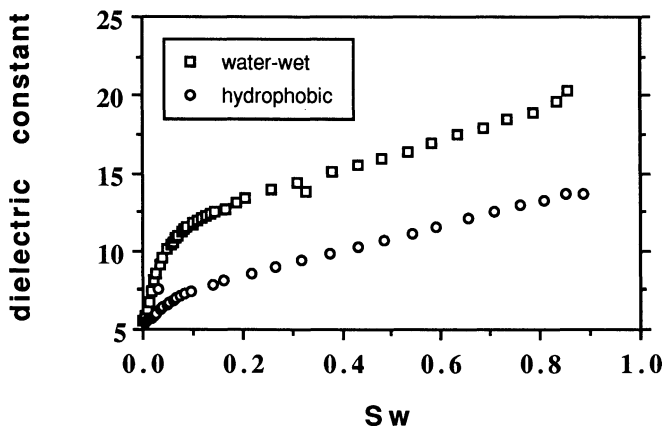


FIG. 5. Dielectric constant of Delaware Brownstone versus the level of water saturation S_w . Data were collected on the original water-wet sample; and after chemical treatment was applied to make the sample hydrophobic.

the data across the entire saturation range approximately parallel the trend of the higher saturation region in the data for the water-wet sample.

Figure 4 shows the data for Berea. We conclude from this data set that the same differences exist between the data for the water-wet and hydrophobic sample. There does appear to be some residual effect in the low saturation region remaining in the data for the treated sample. This may be caused by some variability in the effectiveness of the chemical treatment.

Figure 5 contains the data for Delaware Brownstone. In this sample, the chemical treatment has reduced the magnitude of the increase in K' in the low saturation region, but it is still possible to see the two regions in the data for the treated sample. This again suggests incomplete treatment of the solid surface.

The data collected on the four sandstone samples are very similar in form. The first data set collected on each water-wet sample exhibits the usual form of dielectric data, with the increase in K' at low saturations attributed to rock/water interaction. When the samples are chemically treated to make the solid surface hydrophobic, there is a significant reduction in the magnitude of this low saturation effect. In two of the samples (Beaver and Indiana Light) the low saturation region in the data has been completely eliminated. In the other two samples, the increase in the low saturation region has been reduced but not totally eliminated, suggesting some variation in the success of the chemical treatment.

MODELING OF THE DATA

The dielectric constant of a water-wet sandstone has been found to vary with water saturation in such a way that two regions can be identified in the data, separated at some critical saturation point S_w^0 . The dielectric constant exhibits approximately linear dependence on S_w in both regions with greater slope in the region at lower saturations. The behavior at the lower saturations has been attributed to rock/water interactions. To model the variation in K' of a sandstone as a function of S_w , using the volume fractions and dielectric constants of the three components (rock, water, and air), the interaction between the rock and water has to be accounted for. This can be done by redefining the system and using the wetted rock parameters as was done in Knight and Endres (1990). Alternatively, we suggest that we can eliminate rock/water interaction by chemically treating the rock; and then predict the resulting dielectric constant using as input parameters the dielectric constant of the dry rock, the water, and the air.

We have modeled the experimental dielectric data using CRIM

$$\sqrt{K^*} = (1 - \phi) \sqrt{K_m^*} + S_w \phi \sqrt{K_w^*} + (1 - S_w) \phi \sqrt{K_a^*},$$

where K^* is the measured complex dielectric constant of the sandstone; and subscripts m , w , and a refer to the rock matrix, water, and air respectively. In the case of water-wet samples, the matrix is defined as the wetted rock. For modeling the data from hydrophobic samples, the matrix is taken to be the dry rock. In modeling K' , the complex dielectric constant of each component is used; therefore conductivity contributes to the parameter of interest, K' , and is accounted for in using CRIM.

The input parameters for modeling the water-wet data using the approach described in Knight and Endres (1990) are given in Table 3. The matrix in this case is defined as the wetted rock which is the dry rock plus the surface water coating the solid in the saturation region $0 < S_w < S_w^0$. Table 3 shows the values of the dielectric constant of the matrix K'_m , and the electrical conductivity of the matrix σ_m , for the four sandstones. These parameters were determined from the measurements made at $S_w = S_w^0$, the value of which is also given in Table 3 for each sample. The dielectric constant of the distilled water is 80; the electrical conductivity of the water is 5.0×10^{-5} S/m. The air has a dielectric constant of 1 and zero conductivity. With the surface water included as part of the solid component, the porosity used to determine the volume fractions of water and air must be corrected. The corrected porosity ϕ_c , given by the following expression

$$\phi_c = \phi - S_w^0 \phi,$$

is listed in Table 3 for each of the samples.

The results of modeling the water-wet data with CRIM and the input parameters from Table 3 are shown in Figures 6 through 9. As can be seen, by defining each sample as composed of the wetted rock, water, and air, excellent agreement can be found between data and theory in the region $S_w^0 < S_w < 1.0$.

Table 3. Input parameters for modeling water-wet samples.

Sample	S_w^0	ϕ_c	K'_m	σ_m (S/m)
Beaver	.0742	.0778	6.845	.8805e-4
Indiana Light	.0776	.2370	9.957	.2141e-3
Berea 100	.0787	.1793	10.287	.2818e-4
Delaware Brownstone	.1342	.1108	14.511	.6516e-3

S_w^0 —critical saturation point, ϕ_c —corrected porosity, K'_m —dielectric constant of wetted rock, σ_m —conductivity of wetted rock.

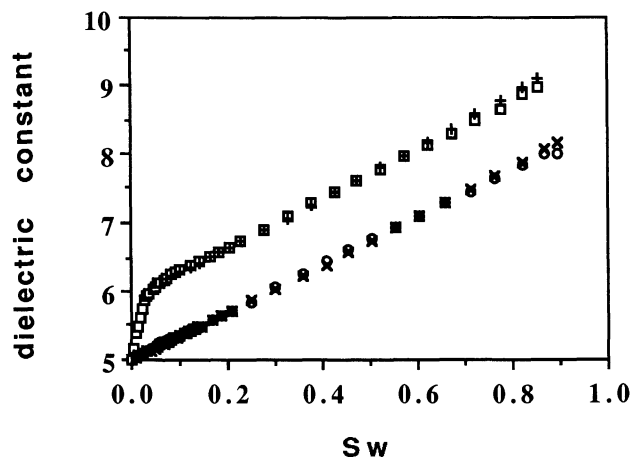


FIG. 6. The results of modeling the dielectric data for Beaver Sandstone using CRIM. The water-wet data (open squares) are modeled (+) with the input parameters given in Table 3. The hydrophobic data (open circles) are modeled (x) with the input parameters given in Table 4.

Instead of incorporating rock/water interaction in the modeling of the data, the chemical treatment of the solid surface was used to eliminate the interaction from the data. With this interaction eliminated, it should be possible to accurately model the dielectric behavior of a rock/water system across the entire saturation range $0 < S_w < 1.0$ using as input only the properties and volume fractions of the dry rock, the water, and the air. This is the approach taken in modeling the data for Beaver, Indiana Light, and Berea. For these three hydrophobic samples, the matrix is defined as the dry rock, with the matrix parameters determined from the measured data at $S_w = 0$. The dielectric constant K'_m and the conductivity σ_m of the dry rock matrix for each of the sandstone samples is given in Table 4. In the case of Delaware Brownstone, it was apparent from the data that the

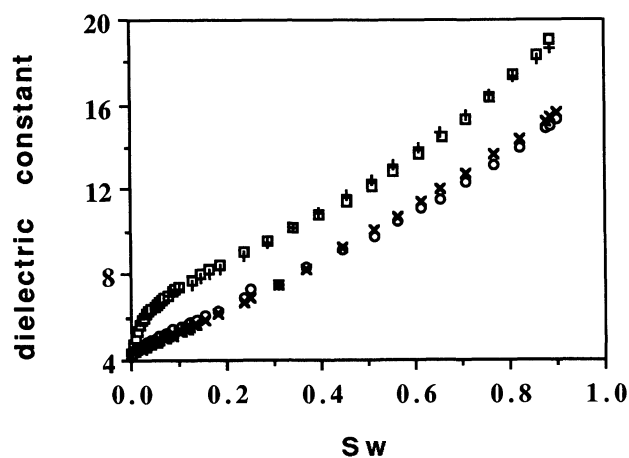


FIG. 7. The results of modeling the dielectric data for Indiana Light Sandstone using CRIM. The water-wet data (open squares) are modeled (+) with the input parameters given in Table 3. The hydrophobic data (open circles) are modeled (x) with the input parameters given in Table 4.

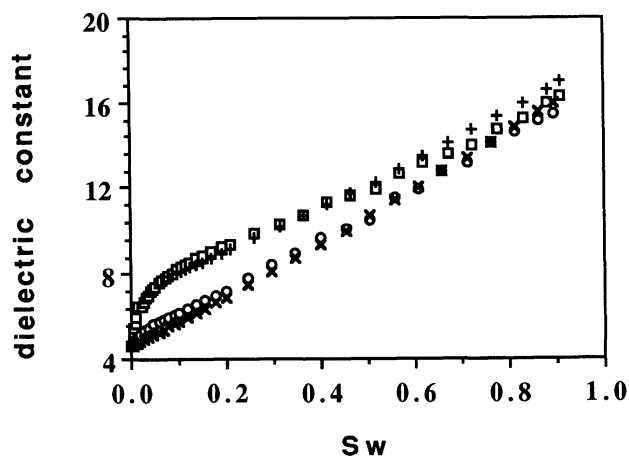


FIG. 8. The results of modeling the dielectric data for Berea Sandstone using CRIM. The water-wet data (open squares) are modeled (+) with the input parameters given in Table 3. The hydrophobic data (open circles) are modeled (x) with the input parameters given in Table 4.

rock/water interaction was not completely eliminated in the "hydrophobic" sample, so the matrix parameters were determined from data collected at $S_w = 0.083$. Also given in Table 4 is the conductivity of the saturating fluid. Although the hydrophobic samples were saturated with distilled water with an electrical conductivity of 5×10^{-5} S/m, the chemical treatment caused an increase in the conductivity of the pore fluid that had to be included in the modeling of the data. The chemical treatment becomes unstable over time and the increased conductivity is most likely caused by the dissolution of chromium ions or complexes.

The results of modeling the data from the hydrophobic samples are also given in Figures 6 through 9. For the three sandstones for which the chemical treatment was most effective, there is excellent agreement between the measured data and the model. The modeling of the data for Beaver (Figure 6), Indiana Light (Figure 7), and Berea (Figure 8) can be accomplished by assuming a system composed of dry rock, water, and air. When interaction between rock and water is eliminated, the dielectric response of partially saturated sandstones becomes surprisingly simple and can be modeled with a three component mixing law that includes only the dielectric constants and volume fractions of the components.

The modeling of the data for the treated sample of Delaware Brownstone is shown in Figure 9. In this case, there is still some residual effect of rock/water interaction at low saturations on the dielectric response. By defining the matrix

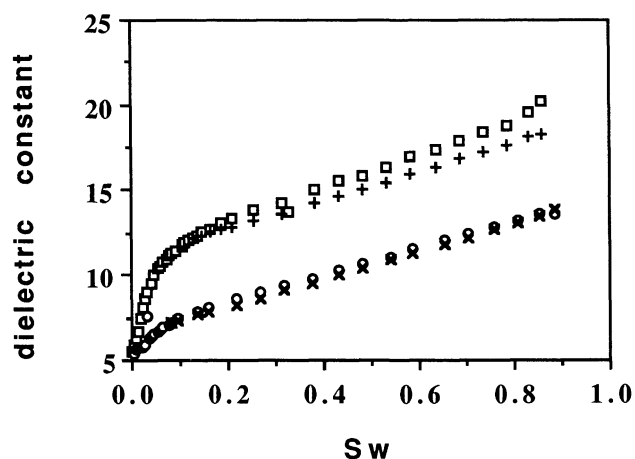


FIG. 9. The results of modeling the dielectric data for Delaware Brownstone using CRIM. The water-wet data (open squares) are modeled (+) with the input parameters given in Table 3. The hydrophobic data (open circles) are modeled (x) with the input parameters given in Table 4.

Table 4. Input parameters for modeling hydrophobic samples.

Sample	K'_m	σ_m	σ_w (S/m)
Beaver A	5.400	.3677e-5	.015
Indiana Light	5.906	.5412e-5	.005
Berea 100	5.857	.6290e-5	.020
Delaware Brownstone	8.420	.7715e-4	.015

K'_m —dielectric constant of dry rock, σ_m —conductivity of dry rock, σ_w —conductivity of saturating fluid..

as the rock solid at $S_w = 0.083$, this rock/water interaction is accounted for. It can be seen from the form of the data that if dry rock parameters were used the model would underestimate the measured dielectric constant. In comparing the results from this sandstone before and after chemical treatment, it can be seen that both the magnitude of the interaction and the saturation range over which it occurs have been reduced.

CONCLUSIONS

Experiments on hydrophobic rock samples have confirmed that changes in the dielectric constant of a sandstone at low saturations are caused by rock/water interaction. When rock/water interaction is eliminated by chemical treatment to create hydrophobic rock surfaces, the low saturation effect is removed, and the dielectric response of a rock containing water can be modeled very simply as a combination of dry rock, water, and air. This is in distinct contrast to water-wet rocks, for which the rock/water interaction must be accounted for to predict the magnitude of the dielectric response.

The experimental results from this study suggest that dielectric measurements, in the laboratory or in the field, are sensitive to the state of the rock/water interface and may prove to be a useful means of determining whether water or some other fluid or chemical species is adsorbed to the solid surface. In applications in the oil industry, borehole measurements of the dielectric constant may be a way of distinguishing between water-wet and oil-wet formations. In groundwater contamination problems, dielectric constant values, determined from well measurements or from ground penetrating radar data, may be an indicator of chemical adsorption at rock surfaces. This study has clearly shown that the chemical nature of the surface of the pore space is a significant factor in determining the dielectric response of sandstones.

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