

The effects of salinity on low-frequency dielectric dispersion in liquid-impregnated porous solids

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 L619

(<http://iopscience.iop.org/0953-8984/7/45/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 22:24

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

The effects of salinity on low-frequency dielectric dispersion in liquid-impregnated porous solids

B Nettelblad† and G A Niklasson‡

† Physics Department, Chalmers University of Technology, S-412 96 Göteborg, Sweden

‡ Teknikum, Uppsala University, Box 534, S-751 21 Uppsala, Sweden

Received 30 August 1995

Abstract. In this letter we study the dielectric properties of brine-impregnated artificial sandstones. The frequency-dependent dielectric permittivity shows a relaxation due to the electrochemical double layer at the interfaces. Good agreement was obtained with a theoretical expression, rigorously valid for dilute colloidal suspensions. The relaxation frequency and amplitude displayed clear dependences on brine conductivity. At the highest liquid conductivities studied, electrode effects were observed at low frequencies.

A lot of theoretical [1–8] as well as experimental [9–14] work has been devoted to the study of the dielectric properties of dilute colloidal suspensions of particles in an electrolyte. It has been found that the electrochemical double layer around the particles gives rise to a relaxation at low frequencies. Many elaborate theories exist, but several of them predict a dependence that can be approximated by the expression [15, 16]

$$\epsilon' - i\epsilon'' = \frac{A}{1 + \sqrt{2i\omega\tau} + i\omega\tau} + \epsilon_\infty \quad (1)$$

where ϵ_∞ denotes the permittivity at high frequencies (due to other relaxations). The relaxation frequency, $f_0 = 1/2\pi\tau$, is in the case of dilute suspensions, roughly

$$f_0 = \frac{D}{\pi a^2} \quad (2)$$

Here, D is the diffusion constant and a the radius of the particles. Even if experimental results agree qualitatively with the theoretical predictions, there can be considerable quantitative disagreement, both in relaxation strength and in relaxation frequency [12, 13, 17, 18]. Ideas such as the ‘hairiness’ of the particle surface [11, 19, 20] or interface conduction in the inner part of the double layer [6, 21] have been employed to explain the discrepancies.

Most of the published theoretical work has been restricted to dilute suspensions. In one study on more concentrated suspensions [7], it is shown that the relaxation frequency is strongly dependent on the concentration of the solid phase. In fact, it is shown that for solid-phase volume fractions above 40%, i.e., in the region where we also encounter porous solids, the relaxation frequency can exceed the value in equation (2) by a factor of 1000 or more. The exact value of the relaxation frequency is dependent on the strength of the electrolyte; such a dependence has already been found theoretically for dilute suspensions

[3]. Porous solids also have high solid-phase volume fractions. Here, the solid phase is connected throughout the material but, otherwise, there is no principal difference to colloidal suspensions. The electrical properties of porous materials are of great interest. For example, sedimentary rocks can contain crude oil and natural gas as well as water, meaning that dielectric measurements can be used for oil exploration [22]. In electrical insulation systems, oil-impregnated paper is prevalent. For brine-saturated rocks, high values of the permittivity have been found [23, 24], that cannot be dismissed as 'electrode effects'. We have previously measured such effects for artificial sandstone samples [25] and found that the permittivity did not seem to have a clear dependence on sample thickness. We have also investigated samples made of sintered polypropylene beads, impregnated with mono- and di-benzyl toluenes containing tetraisoamylammonium picrate [26]. For such samples, we found that we could get a good agreement between the experimental permittivity and equation (1).

We were not able to use data from our polypropylene-toluene systems to ascertain the dependence on the liquid conductivity. The relaxation frequency was too low at room temperature, and the highest liquid conductivity attainable was so low that we could not achieve a wide range of conductivities. However, for salty water, the relaxation frequency is higher (due to the higher diffusion constant), and it is possible to vary the conductivity in a wide range.

In this letter we discuss the dependence of the dielectric dispersion in porous solids due to interface effects on the conductivity of the pore liquid. The experimental results are obtained from measurements on artificial sandstone samples, impregnated with salty water. These samples have been described earlier [27, 28]. They were composed of Danish beach sand, glued together with small amounts of epoxy (about 2–3% by volume) and subjected to pressure before the epoxy was cured. The sand contained 87% quartz, 7% plagioclase and 6% of k-feldspar. The samples were prepared to attain a log-normal distribution of grain diameters with a medium value of 0.25 mm. The samples were impregnated in a vacuum chamber, that was evacuated to 0.1 Torr before letting the slightly saline water into it. The measurements were taken between 5 Hz and 13 MHz using an HP 4192 A impedance analyser. The samples were placed in a test cell between brass electrodes, using a guard electrode to eliminate effects from conduction on the outer surface of the samples. The electrodes were mounted on plastic screws, which enabled us to make measurements on specimens with different thicknesses. This arrangement also gave good contact between the sample and the electrodes.

In figure 1, we present the measured permittivity of a typical sample as a function of frequency for four different values of the liquid conductivity. The low-frequency permittivity clearly increases and the relaxation shifts to higher frequencies with increasing strength of the electrolyte. We differentiated the curves in figure 1 numerically, by using a five-point formula to eliminate effects of the higher derivatives (except at the ends where we used a three-point formula). Since we differentiated the $\log \epsilon'$ versus \log frequency curve, differences due to different relaxation amplitudes were eliminated.

The results from the differentiation are plotted in figure 2. We observe a clear dependence on liquid conductivity. In figure 2, we also give the corresponding derivative of equation (1) for a typical relaxation frequency 30 Hz (solid line). Note the strong resemblance of the experimental curves and the theoretical curve for low liquid conductivities. This supports the validity of equation (1). For the highest frequencies, we experimentally observe deviations from the expected constant value of -1.5 . Since the value of $\tan \delta$ (the dielectric loss factor) is very high at these frequencies, the permittivity values

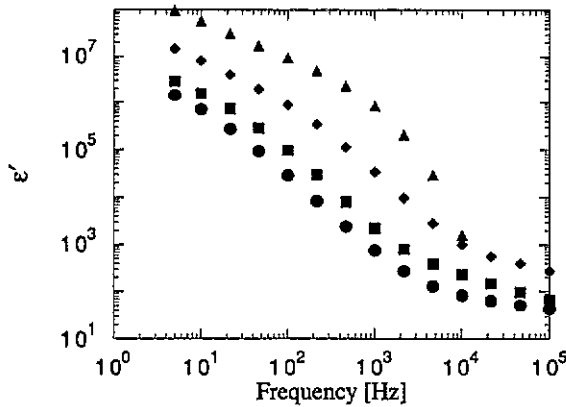


Figure 1. The measured apparent dielectric permittivity of a typical sample (39% porosity) as a function of frequency for the liquid conductivities 0.8 mS m^{-1} (circles), 11 mS m^{-1} (squares), 0.12 S m^{-1} (diamonds), and 1.0 S m^{-1} (triangles).

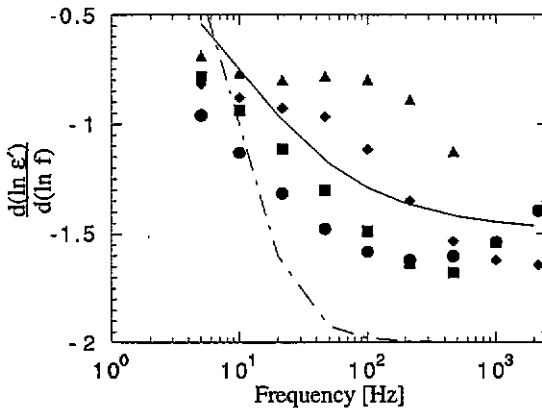


Figure 2. Differentiated values $d(\ln \epsilon')/d(\ln f)$ as functions of frequency for the sample of figure 1 (same notation as in figure 1). The solid line is the differentiation of equation (1) ($f_0 = 10 \text{ Hz}$) and the chain-dotted line is the differentiation of the Debye dependence ($f_0 = 10 \text{ Hz}$).

are somewhat uncertain. We may also have interference from other relaxation processes. The values of the derivative are thus not accurate for those frequencies.

Strong deviations from the theory are noticeable at low frequencies for the measurements at the two highest liquid conductivities. It is tempting to explain this in terms of the occurrence of a second relaxation process at these frequencies. It is seen that the curve for the highest liquid conductivity in figure 2 displays an almost constant value at low frequencies. This signifies a power-law behaviour of the dielectric permittivity with an exponent in the range 0.7–0.8. Such behaviour is very common for the dielectric response of metal electrodes in an electrolyte [29,30]. Hence, we believe that this low-frequency power-law response is due to polarization effects at the contacts. (We have obtained exponents around 0.8–0.9 when making measurements on the liquid alone.) Evidence for this interpretation is shown in figure 3. We cut one specimen into several samples of different thicknesses. If the original specimen was macroscopically homogeneous, the samples should

have the same bulk properties. In figure 3, the measured dielectric permittivity and AC conductivity are shown as functions of frequency for two samples from the same specimen, having different sample thicknesses (5.1 mm and 3.5 mm). The measurements were taken at two different values of the liquid conductivity: 0.23 S m^{-1} and 2.3 mS m^{-1} . We see that both the permittivity and the conductivity appear to be the same for the two samples at the lower value of the liquid conductivity. Hence, it seems as if the measured results are due to 'bulk' effects. For the higher value of the liquid conductivity, however, the measured permittivity and conductivity values are not equal at the lowest frequencies. Actually, the measured capacitance and conductance are almost the same for the two samples at the lowest frequencies, suggesting that electrode effects are dominant here. Note, however, that the differences appear to decrease at higher frequencies, suggesting that bulk effects gradually become more important.

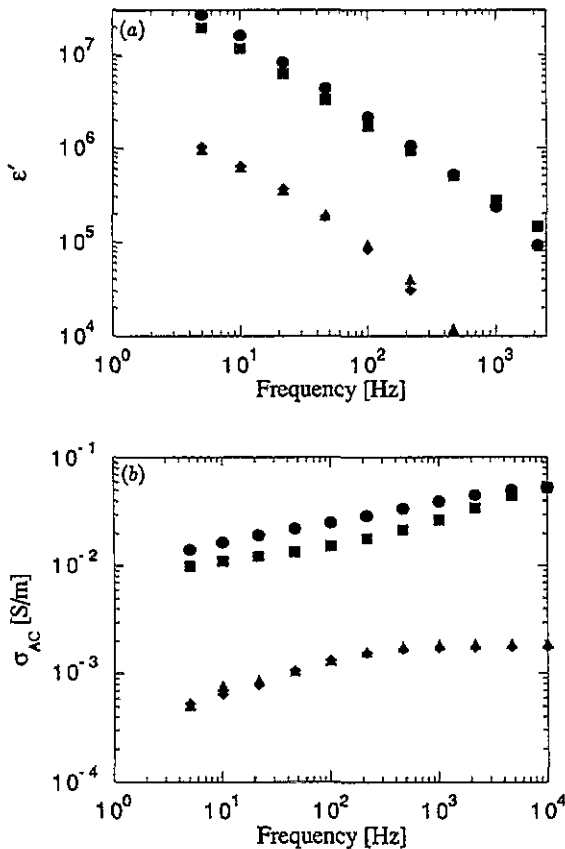


Figure 3. The measured permittivity (a) and AC conductivity (b) of a 44%-porosity specimen cut into two samples of different thicknesses. The liquid conductivity was 0.23 S m^{-1} for a 5.1 mm sample (circles) and a 3.5 mm sample (squares); and was 2.3 mS m^{-1} for a 5.1 mm sample (diamonds) and a 3.5 mm sample (triangles).

The effect of electrode interfaces may, according to some theories [31, 32], be modelled as an equivalent circuit consisting of an ideal capacitor in parallel with an ideal resistor. This circuit is connected in series with the sample. Assuming a similar model for the

sample, this addition would yield a Debye-type relaxation. Since our high-frequency data in figure 2 seem to show a somewhat steeper slope than -1.5 , we also included the theoretical differentiation of a Debye dependence in figure 2. Note that a Debye relaxation is incompatible with the experimental data.

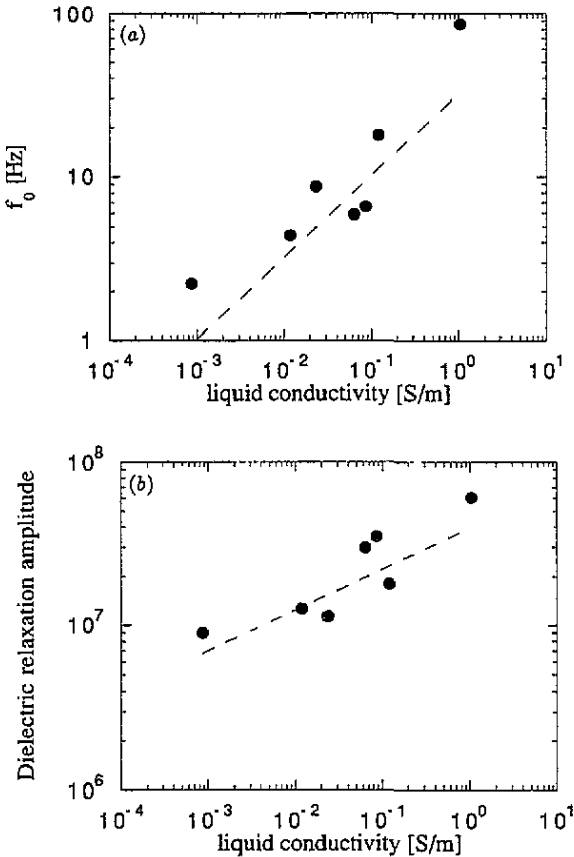


Figure 4. The estimated relaxation frequency (a) and relaxation amplitude (b) (according to equation (1)) of the 39% porosity sample in figures 1 and 2. The dashed lines are computer fits to the dependences $f_0 \propto \sigma_{liquid}^{0.5}$ and $A \propto \sigma_{liquid}^{0.25}$.

Restricting ourselves to the part of the experimental data that appears to be due to a relaxation process that can be described by equation (1), we use computer fits to extract values for the relaxation frequencies and amplitudes. In figure 4(a), we show the relaxation frequency as a function of the liquid conductivity, σ_{liquid} . Although there is some scattering, the relaxation frequency displays a clear dependence on the liquid conductivity. As the liquid's conductivity is increased, the relaxation frequency increases too. The amplitude factor, A , is presented in figure 4(b). Here too we get an increase with increasing liquid conductivity; however, the dependence is much weaker. Figure 4 seems to indicate that power laws would give reasonable approximations to the results. Actually, good agreement is obtained by $f_0 \propto \sigma_{liquid}^{0.5}$ and $A \propto \sigma_{liquid}^{0.25}$. Although it must be stressed that the data are too limited for drawing any definite conclusions about the exact dependence, it is interesting

that those exponents yield the following result for frequencies far above the relaxation frequency: $\epsilon' \propto \sigma_{\text{liquid}}/\omega^{-1.5}$, which motivates the use of the so called reduced frequency [33–35] to display data measured at different liquid conductivities.

In conclusion, we have found that a low-frequency relaxation found in dielectric measurements on impregnated artificial 'rocks' is shifted upwards in frequency as the conductivity of the impregnation liquid is increased. The relaxation amplitude is also increased, although the dependence is weaker. The frequency dependence can be fitted with an expression describing electrochemical double-layer effects in a dilute suspension. The validity of this expression for porous materials may seem surprising, and a rigorous theoretical justification cannot be given at present. The indication is that the relaxation is due to the electrochemical double layer. For high values of the liquid conductivity, the data seem to display a second relaxation. We suggest that this second relaxation is due to the electrodes.

References

- [1] Schwarz G 1962 *J. Phys. Chem.* **66** 2636–42
- [2] Fixman M 1980 *J. Chem. Phys.* **72** 5177–86
- [3] DeLacey E H B and White L R 1981 *J. Chem. Soc. Faraday Trans. II* **77** 2007–39
- [4] Chew W C and Sen P N 1982 *J. Chem. Phys.* **77** 4683–93
- [5] Grosse C and Foster K 1987 *J. Phys. Chem.* **91** 3073–6
- [6] Rosen L A, Baygents J C and Saville D A 1993 *J. Chem. Phys.* **98** 4183–94
- [7] Shilov V N and Borkovskaya Y B 1994 *Colloid. J. (Engl. Transl.)* **56** 724–9
- [8] Raziilov I A, Pendze G, Lyklema J and Dukhin S S 1994 *Colloid. J. (Engl. Transl.)* **56** 736–44
- [9] Schwan H P, Schwarz G, Maczuk J and Pauly H 1962 *J. Phys. Chem.* **66** 2626–35
- [10] Springer M M, Korteweg A and Lyklema J 1983 *J. Electroanal. Chem.* **153** 55–66
- [11] Rosen L A and Saville D A 1990 *J. Colloid Interface Sci.* **140** 82–92
- [12] Carrique F, Zurita L and Delgado A V 1994 *Colloid. Surf. A* **92** 9–21
- [13] Carrique F, Zurita L and Delgado A V 1994 *J. Colloid Interface Sci.* **166** 128–32
- [14] Blum G, Maier H, Sauer F and Schwan H P 1995 *J. Phys. Chem.* **99** 708–89
- [15] Mandel M and Odijk T 1984 *Rev. Phys. Chem.* **35** 75–108
- [16] Nettelblad B and Niklasson G A unpublished
- [17] Myers D F and Saville D A 1989 *J. Colloid Interface Sci.* **131** 461–70
- [18] Rosen L A and Saville D A 1991 *Langmuir* **7** 36–42
- [19] van der Put A G and Bijsterbosch B H 1983 *J. Colloid Interface Sci.* **92** 499–507
- [20] Rosen L A and Saville D A 1992 *J. Colloid Interface Sci.* **149** 542–52
- [21] Kijlstra J, van Leeuwen H P and Lyklema J 1993 *Langmuir* **9** 1625–33
- [22] Poley J P, Nooteboom J J and de Waal P J 1978 *Log Analyst* **19** 8–30
- [23] Lockner D A and Byerlee J D 1985 *J. Geophys. Res.* **90** 7837–47
- [24] Ruffet C, Gueguen Y and Darot M 1991 *Terra Nova* **3** 265–75
- [25] Nettelblad B and Niklasson G A 1994 *Solid State Commun.* **90** 201–4
- [26] Nettelblad B unpublished
- [27] Fjær E, Holt R M, Rathore J S and Åhlén B 1991 *Geophys. J.* **107** 687–91
- [28] Åhlén B 1993 *Licentiate Thesis* Chalmers University of Technology
- [29] Pajkossy T 1994 *J. Electroanal. Chem.* **364** 111–25
- [30] de Levie R 1990 *J. Electroanal. Chem.* **281** 1–21
- [31] Macdonald J R 1974 *J. Chem. Phys.* **61** 3977–96
- [32] Archer W I and Armstrong R D 1980 *Electrochemistry* vol 7, ed H R Thirsk (London: The Chemical Society)
- [33] Holwech I and Nøst B 1989 *Phys. Rev. B* **39** 12 845–52
- [34] Nøst B, Hansen B D and Haslund E 1992 *Phys. Scr. T* **44** 67–70
- [35] Nettelblad B and Niklasson G A 1995 *Phys. Rev. B* submitted