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SONIC AND RESISTIVITY MEASUREMENTS ON BEREA SANDSTONE CONTAINING TETRAHYDROFURAN HYDRATES: A POSSIBLE ANALOGUE TO NATURAL GAS HYDRATE DEPOSITS

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ABSTRACT

Deposits of natural gas hydrates exist in arctic sedimentary basins and in marine sediments on continental slopes and rises. However, the physical properties of such sediments, which may represent a large potential energy resource, are largely unknown. In this paper, we report laboratory sonic and resistivity measurements on Berea sandstone cores saturated with a stoichiometric mixture of tetrahydrofuran (THF) and water. We used THF as the guest species rather than methane or propane gas because THF can be mixed with water to form a solution containing proportions of the proper stoichiometric THF and water. Because neither methane nor propane is soluble in water, mixing the guest species with water sufficiently to form solid hydrate is a difficult experimental problem, particularly in a core. Because THF solutions form hydrates readily at atmospheric pressure it is an excellent experimental analogue to natural gas hydrates.

Hydrate formation increased the sonic P-wave velocities from a room temperature value of 2.5 km/s to 4.5 km/s at -5°C when the pores were nearly filled with hydrates. Lowering the temperature below -5°C did not appreciably change the velocity however. In contrast, the electrical resistivity increases nearly two orders of magnitude upon hydrate formation and continues to increase more slowly as the temperature is further decreased. In all cases the resistivities are nearly frequency independent to 30 kHz and the loss tangents are high, always greater than 5. The dielectric loss shows a linear decrease with frequency suggesting that

ionic conduction through a brine phase dominates at all frequencies, even when the pores are nearly filled with hydrates. We find that the resistivities are strongly a function of the dissolved salt content of the pore water. Pore water salinity also influences the sonic velocity, but this effect is much smaller and only important near the hydrate formation temperature.

Introduction

Hydrates are a crystalline form of water containing voids or cavities that can trap other (guest) molecules which play an important role in stabilizing the hydrate structure. Two types of hydrates (types 1 and 2) are known to form. The first type contains only relatively small cavities (>8.6 Å in diameter) that can trap guest species smaller than ethane, while the second contains a mixture of small and large (9.5 Å in diameter) cavities and can trap molecules as large as isobutane. Most of the common constituents of natural gas form hydrates, usually type 1, but type 2 hydrates can also form if significant amounts of C_3H_8, C_4H_{10}, or CO_2 are present.

Until recently, natural gas hydrates were widely known only as a nuisance which condensed in gas transmission lines. Then Russian investigators reported natural gas hydrate deposits in the Siberian arctic. These early reports were confirmed with the discovery of large natural gas hydrate deposits in arctic North America and in marine sediments. Research interest in hydrates increased as hydrates became not only a potential engineering problem in the arctic, but also a potential energy resource. However, surprisingly little is known about the physical properties of sediments containing hydrates in their pores and except for the pioneering work by Stoll and Bryant (1979), few laboratory measurements have been reported.

In this paper, we present laboratory sonic and resistivity measurements on Berea Sandstone cores containing tetrahydrofuran (THF) hydrate. Tetrahydrofuran was used as a guest species instead of methane or some other constituent of natural gas because THF hydrate is stable at moderate temperatures (+4°C) and atmospheric pressures, greatly simplifing experimental procedures. A second major advantage of THF hydrate is that the guest is mixable with water. This eliminates the problem of ensuring complete mixing between the guest species and water, which is a formidable problem inside the pore spaces of sedimentary rock. Because the crystal structure of hydrates is largely independent of the guest species, the physical properties of THF hydrate containing samples is probably similar to the physical properties of a natural gas hydrate deposit formed in similar rocks. This is particularly likely if the natural hydrates form from gas containing molecules large enough to form type 2 hydrates.

This paper focuses on sonic and electrical measurements because preliminary calculations (Pearson, 1982) show that sonic velocities and resistivities are more strongly affected by the presence of hydrates than are other physical properties such as densities or thermal conductivities. In addition, seismic and electrical methods are the most commonly applied exploration geophysical techniques. Clearly a detailed understanding of the electrical and acoustic properties of hydrates is necessary to design and interpret geophysical surveys over natural gas hydrate deposits.

Experimental Method

The samples were cylindrical cores approximately 5 cm long and 2.54 cm in diameter cut from a block of Berea sandstone perpendicular to the bedding plane. The ends were ground parallel to ensure good contact between the ends of the samples and the electrodes or transducers. Samples were saturated with a stoichiometric mixture of THF and water (18 parts water to 1 part THF, Gough and Davidson, 1971), under vacuum. As part of the study, various amounts of NaCl were added to the fluid. The concentration of salt is reported by the molarity of the water NaCl solution before THF was added to the mixture. The samples were tightly jacketed in plexiglass or shrink tubing before any measurements were conducted. Because temperature is an important variable in our study all measurements were conducted in a NESLAB RTE-8 constant temperature bath. We left the sample in the bath for 24 hours, well after a temperature change, to ensure the sample had equilibrated with the bath.

The electrical measurements were conducted using the Collett and Katsube (1973) two-electrode system. To reduce polarization effects we saturated the rocks with pore fluid containing known quantities of salt. Because we used a Princeton Applied Research model 5204 lock-in analyzer, which can measure the in-phase and quadrature components of the voltage drop across the precision resistor, we were able to calculate the real and imaginary components of the resistivity, the phase angle, and the complex relative permittivity. The complex electrical properties (i.e. the complex permittivity (K*) and the loss tangent (D) were calculated using the following equations presented by Collett and Katsube, 1973.

$$D = \frac{\rho'}{\sqrt{|\rho^*|^2 - (\rho')^2}} \tag{1}$$

$$K^* = \frac{1}{\omega |\rho^*| \varepsilon_0} \tag{2}$$

where $|\rho^*|$ and ρ' are the magnitude complex resistivity and the real part of the complex resistivity respectively, ω is the frequency and ε_0 is the permittivity of free space. The real (K′) and imaginary (K") parts of the relative permittivity can be calculated from K^* using:

$$K = \frac{K^*}{1+D^2} \tag{3}$$

$$K'' = K^* \left(\frac{D}{1+D^2}\right) \tag{4}$$

Sonic measurements were conducted using the Mattaboni and Schreiber (1967) pulse transmission method. We used Valpey Fisher LIZ-5 quartz 1 MHz piezoelectric transducers that were attached to the sample by a spring-loading device. All measurements (both sonic and electric) were conducted at atmospheric pressure, except for a small axial load, >0.1 MPa that was applied to ensure that the electrode or transducer remained in contact with the sample.

Electrical Results

As shown in Figs. 1 and 2, the resistivities of berea cores containing THF hydrates are functions of both temperature and salinity at which the measurements were made. However, to 30 KHz, the resistivities are nearly independent of frequency. Figures 1 and 2 plot the complex resistivity, but because the imaginary component of the resistivity was always very small, usually less than 10% of the real component, the real and complex resistivities are nearly equal. As a result, loss tangents are very high, often in excess of 100. Both the real relative permittivity and the imaginary part which is proportional to the dielectric loss are linear functions of frequency. The log linear relationship between the dielectric loss and frequency (Fig. 3) is particularly important because the dielectric loss is a parameter that describes the motion of electric charge. If the material displays conduction that arises not from the effect of polarization on the displacement current but from actual charge transport, Hasted (1974) shows that

$$\epsilon = \epsilon_{\text{diaelectric}} + \frac{\sigma}{4\pi\omega\epsilon_0} \qquad (5)$$

Here ϵ dielectric is the component of the dielectric loss associated with loss from polarization currents. With a dielectric loss mechanism such as that from water molecules and in the absence of conductors, ϵ will normally show a strong peak when plotted vs frequency. However, if conduction dominates the polarization effects, ϵ will be inversely proportional to frequency. Thus the slope of the line from Fig. 3, which is (0.994) calculated using least square regression techniques, implies that conduction is much more important than polarization effects in determining the electrical properties of hydrate containing Berea sandstone cores.

The effect of temperature and salinity on the resistivities of the Berea cores also suggests that the electric currents flow because of ionic conduction in an unfrozen brine phase, which is present in the rock even after hydrates start to form. The exponential increase in resistivity with temperature occurs because lowered temperatures cause the proportion of hydrates in the pores to increase, further constricting the brine phase. The decrease in resistivity as the salinity increases (shown in Fig. 2) is caused by an increase in the ionic concentration of the brine phase. The additional ions present probably also inhibit the formation of hydrates increasing the amount of brine present in the pores.

The electrical properties of hydrate containing sediments can be quantitatively understood using Archie's law ($\rho = a\ \rho_w\ \phi^{-m}\ Sw^{-n}$), an empirical relationship between water content and the resistivity of water-saturated sediments. Here ρ is the resistivity of the sediments, ρ_w is the pore water resistivity, Sw is the fraction of the porosity occupied by liquid water, and a, m, and n are empirically derived parameters. This equation also applies to rocks where the pore spaces are partially filled with ice or hydrates. However, as the amount of liquid water decreases, Sw and ρ_w are both reduced, Sw because some of the available pore space is now filled with a solid nonconductor, and ρ_w because the dissolved salts are concentrated in the remaining unfrozen brine. If the brine is not very near saturation, the effect of hydrate or ice formation of ρ_w is relatively easy to quantify because an increase in salt concentration causes a linear decrease in ρ_w. Because hydrates of ice exclude all of the dissolved salts as they form, the salt concentration of the brine inclusions is inversely proportional to the volume fraction of liquid water, if we assume that the sediments were initially water saturated. In addition, the resistivity of aqueous solutions increases exponentially with decreasing temperatures. Including both the temperature and concentration effects, the resistivity of a partially frozen brine at temperature T is thus proportional to $(C)^T$ Sw where C is a constant. Substituting this relationship into Archie's equation and dividing by the resistivity at 0°C, we find that the ratio of frozen (ρ_f) and thawed (ρ_t) resistivities is

$$\rho_f/\rho_t = C^{-T}\ Sw^{1-n} \quad . \tag{6}$$

Archie's law accounts for the rapid decrease in resistivity as a function of temperature (see Fig. 4). Because N is usually equal to 2, the resistivity is inversely proportional to Sw. As the temperature decreases, the concentration of the brine at equilibrium with hydrates increases causing Sw to decrease and the resistivity to increase. Increasing the molarity of the salt solution causes the resistivity to decrease because the increased salinity of the pore water inhibits the formation of hydrates, which increases the amount of unfrozen water (Sw) present.

Seismic Results

Sonic P-wave velocities, measured on hydrate containing Berea sandstone cores as a function of temperature are shown in Fig. 5. This figure shows results from cores saturated with two different NaCl solutions. Note that in both cases the sonic velocities increase from 2.5 km/s to 4.5 km/s when hydrates begin to form in the pore spaces. Once hydrates form, the velocities reach a plateau where further cooling produces very little change.

As shown in Fig. 5 the salinity of the saturating liquid has very little effect on the sonic velocities once hydrates have formed in the cores. However cores saturated with saline water and THF approach the high velocity plateau more gradually than do samples saturated with pure water and THF. Thus the behavior of sonic velocities as a function of temperature contrasts with the electrical resistivity measurements in that electrical resistivities decrease rapidly as a function of temperature even after the pore spaces of the sample are probably nearly full of hydrates, while sonic velocities rapidly increase when hydrates start to form in the pore spaces but then the velocities reach a plateau where further cooling produces very little change in sonic velocities. The difference in the temperature dependence of sonic velocities and resistivities illustrates a fundamental difference in the mechanism by which electrical and acoustic signals are transmitted in rock. Electrical signals are transmitted through the brine phase so electrical properties remain sensitive to the amount of brine present, even when the fraction of the pore volume containing brine becomes very small. In contrast, acoustic pulses are transmitted primarily through the solid matrix so, once the pore volume is largely filled with hydrates a further decrease in the small brine fraction produces only a negligible change in velocity. However the slower asymptotic approach in the brine-rich sample suggests that amount of fluid in the unfrozen brine phase does have some effect on velocity when the brine phase consists of a relatively large amount of fluid.

The compressional velocity of hydrates forming in a sediment can probably be understood using a three-phase time-averaged equation, first proposed by Timur (1968) for partially frozen sediments and since tested by several other authors. The compressional velocity (Vp) is related to the velocity of ice (Vs), the velocity of the brine inclusions (Vb), and the velocity of the solid matrix (Vm) by

$$1/Vp = \frac{\phi\ (S_w)}{Vb} + \frac{(1-S_w)}{Vs} + \frac{(1-\phi)}{Vm}\ , \tag{7}$$

because of the similarities between the seismic velocities of ice and hydrates, this equation can probably be used to calculate the velocity of a mixture of hydrates and brine in sedimentary rock. Note that Eq. 7 depends linearly on S_w, in contrast to Eq. 6 which, if n 2, is inversely proportional. The difference in electrical and sonic properties as a function of temperature can be explained by the difference in the dependence of Eqs. 6 and 7 on S_w. The electrical properties are inversely proportional to S_w so the electrical resistivity remains sensitive to changes in S_w even when very little unfrozen water remains in the rock. In contrast, in Eq. 7 S_w enters directly as a term added to other quantities. Thus as S_w becomes small it has a negligible effect on the seismic velocity.

Conclusions

Several significant conclusions can be drawn from this study: (1) the resistivities and sonic velocities of Berea sandstone cores are strongly affected by the presence of hydrates. Resistivities increased by an order of magnitude and continued to increase rapidly as further decreases in temperature reduced the amount of unfrozen brine present in the rock. The sonic velocities, in contrast, rapidly increased when hydrates began to form in the cores but soon approached a limiting value. Further cooling produced only a very small increase in sonic velocities. (2) The salinity of the pore water in which the hydrates form has a strong affect on the resistivities but a very small affect on the sonic velocities. We suggest that the effect of temperature and salinity on resistivities and sonic velocities can be explained if the samples obey Archie's law for resistivities and the three-phase rule for velocities. (3) Resistivities of hydrate containing cores are nearly frequency independent in the range from 10 Hz to 30 kHz. However, both the dielectric constant and the dielectric loss decrease rapidly as a function of frequency. The log linear relationship between frequency and dielectric loss suggests that the electrical properties of the hydrate containing samples are controlled by ionic conduction in an unfrozen brine phase.

Our experimental results show that the presence of hydrates has a strong affect on the acoustic and electric properties of sediments. An increase of several orders of magnitude in electrical resistivities can easily be detected using a variety of electrical exploration techniques.

Also an 80% increase in sonic velocity is sufficient to produce a very strong reflection in seismic reflection data and can easily be detected in seismic refraction surveys. This very strong velocity contrast may account for strong reflections that are often observed at the bottom of possible hydrate bearing horizons in marine seismic surveys. (Shipley et al 1979).

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Figure Captions

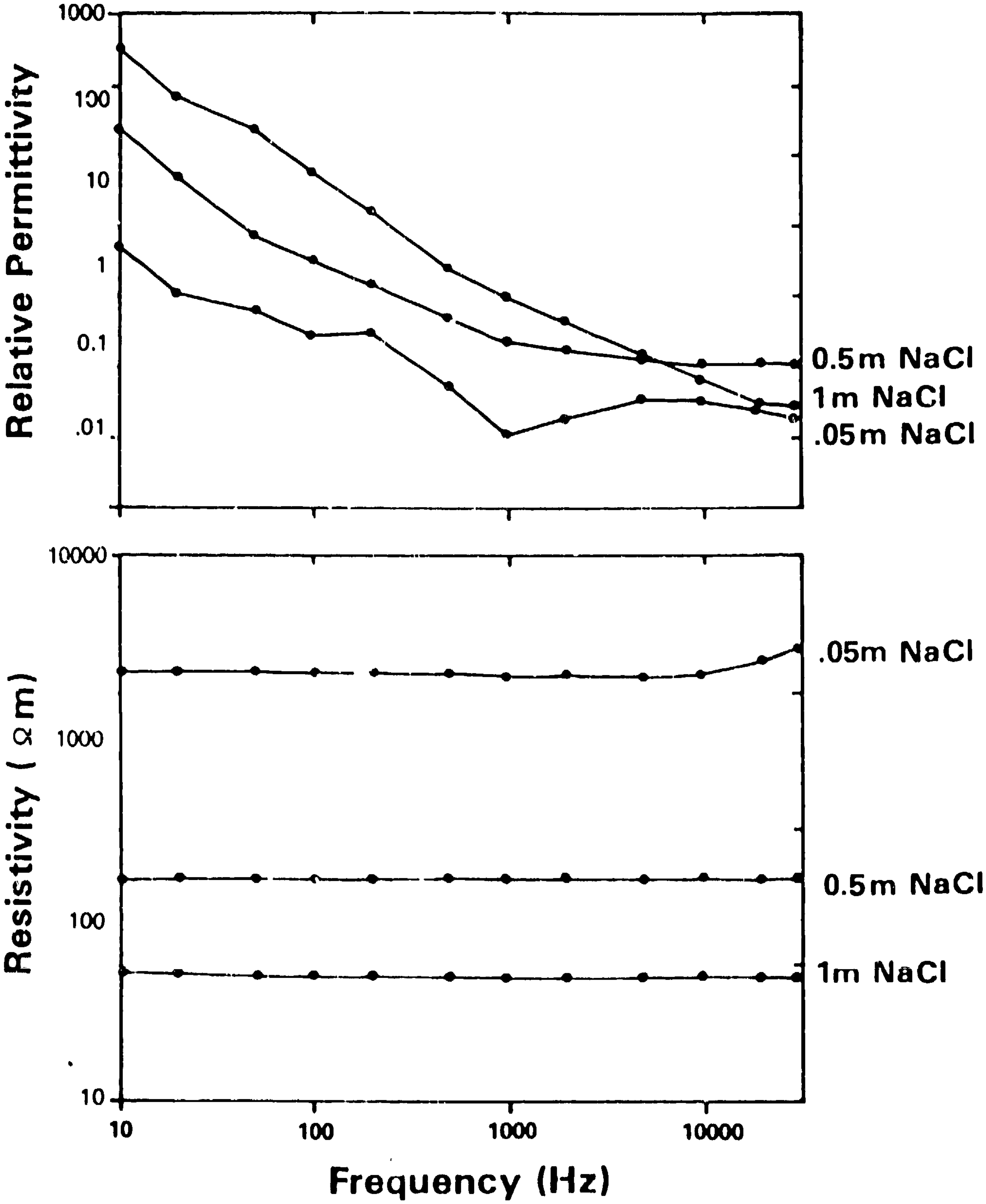
Fig. 1. Resistivity and relative permittivity x 10^{-5} as a function of temperature and frequency for a Berea core saturated with 0.5 N NaCl tetrahydrofuran solution.

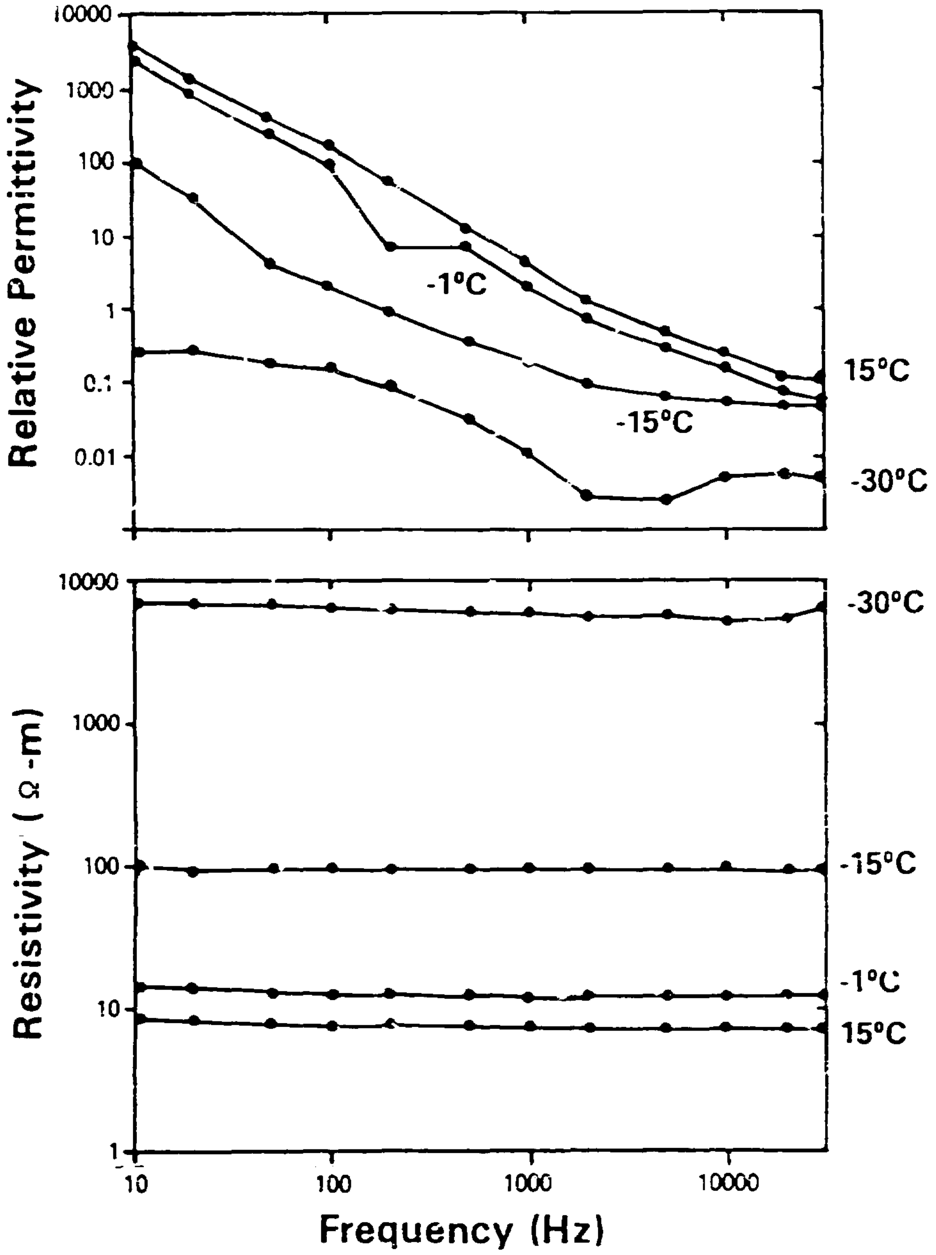
Fig. 2. Resistivity and relative permittivity x 10^{-5} as a function of frequency and salinity at -24°C.

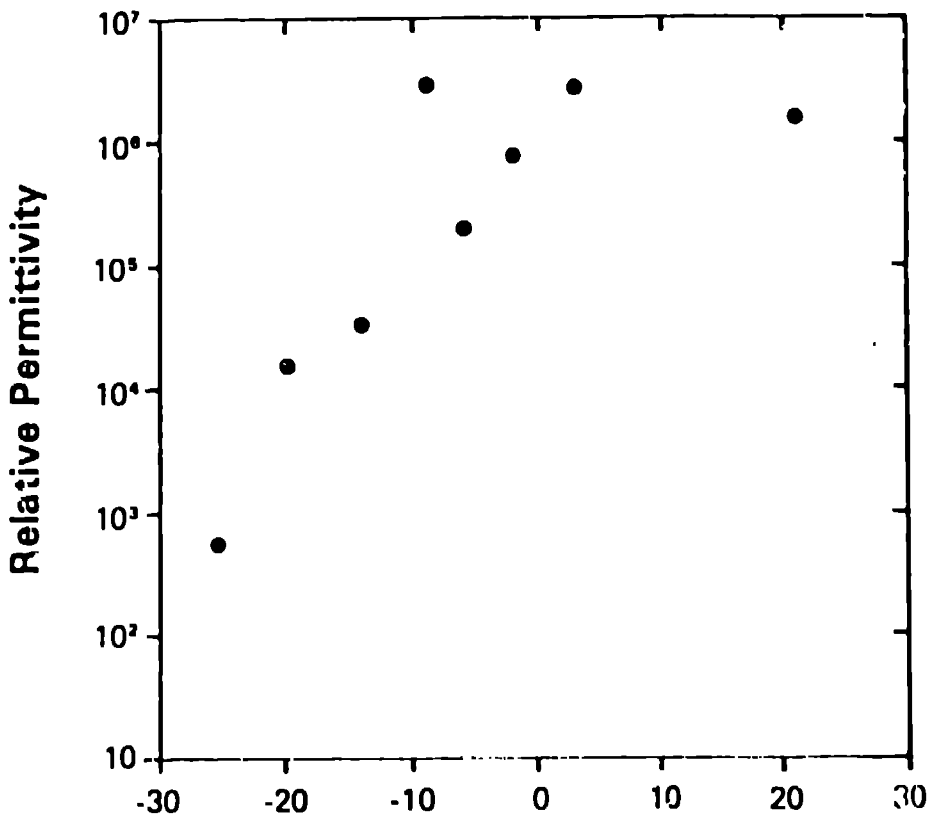
Fig. 3. Imaginary part of the relative permittivity x 10^{-4} vs frequency for a Berea core saturated with a 0.5 N NaCl tetrahydrofuran solution at -24°C.

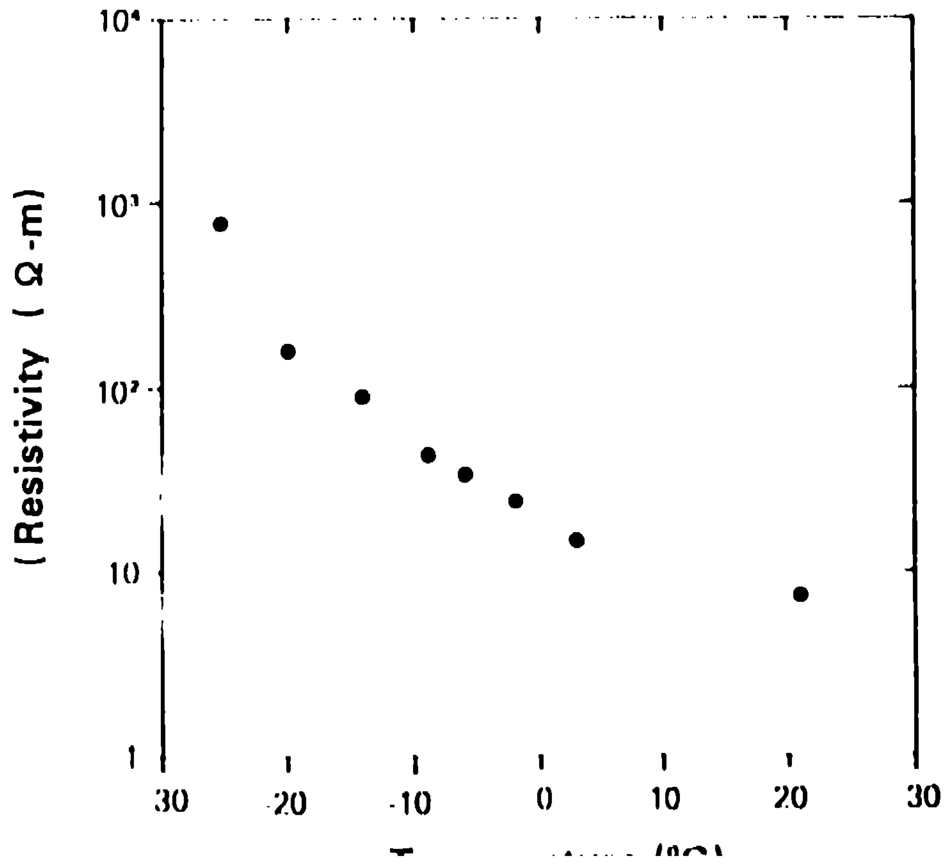
Fig. 4. Resistivity and relative permittivity x 10^{-1} as a function of temperature for a core saturated with a 0.5 N NaCl tetrahydrofuran solution.

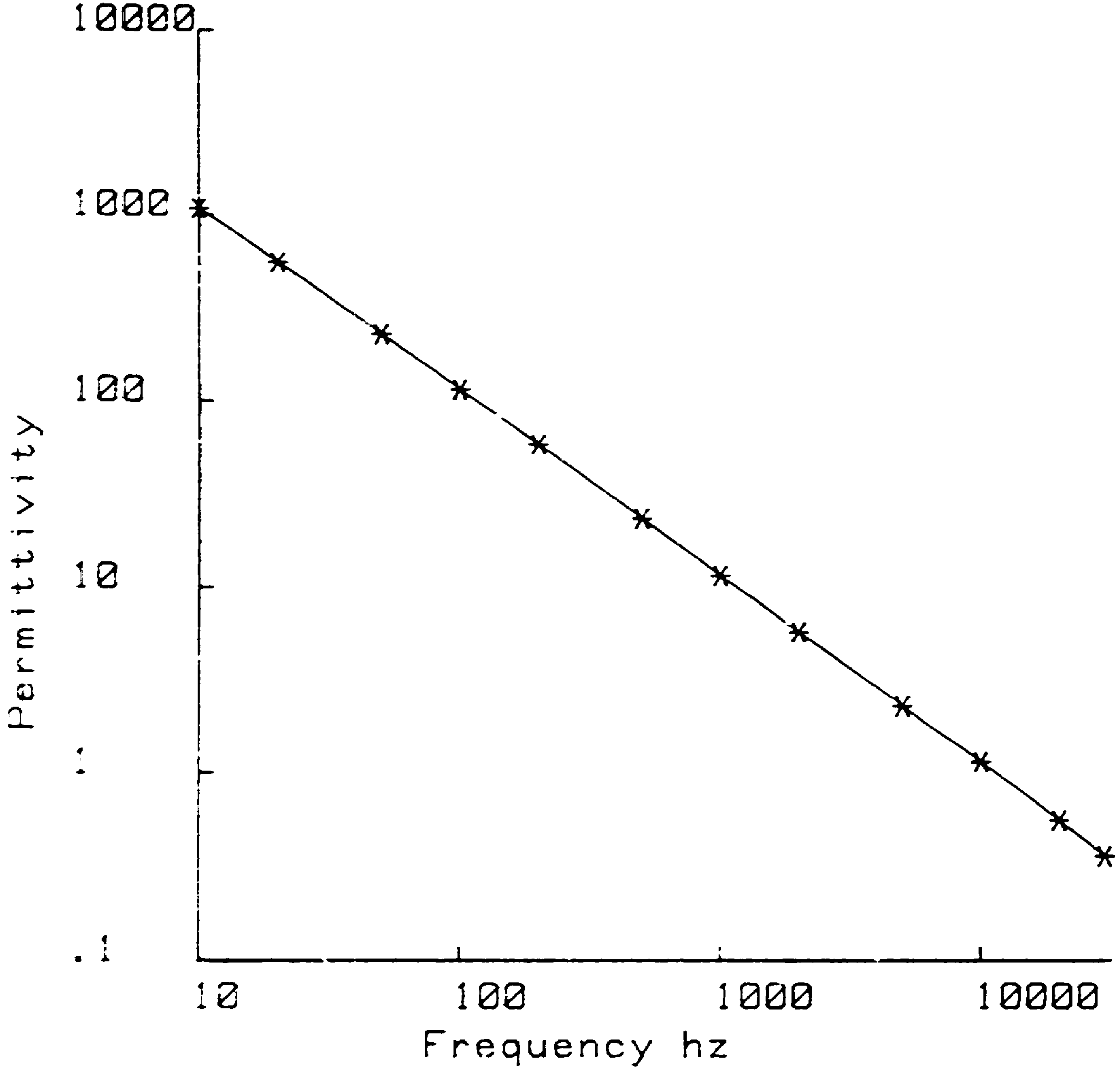
Fig. 5. Sonic velocities vs temperatures for two Berea cores showing the effect of salinity.

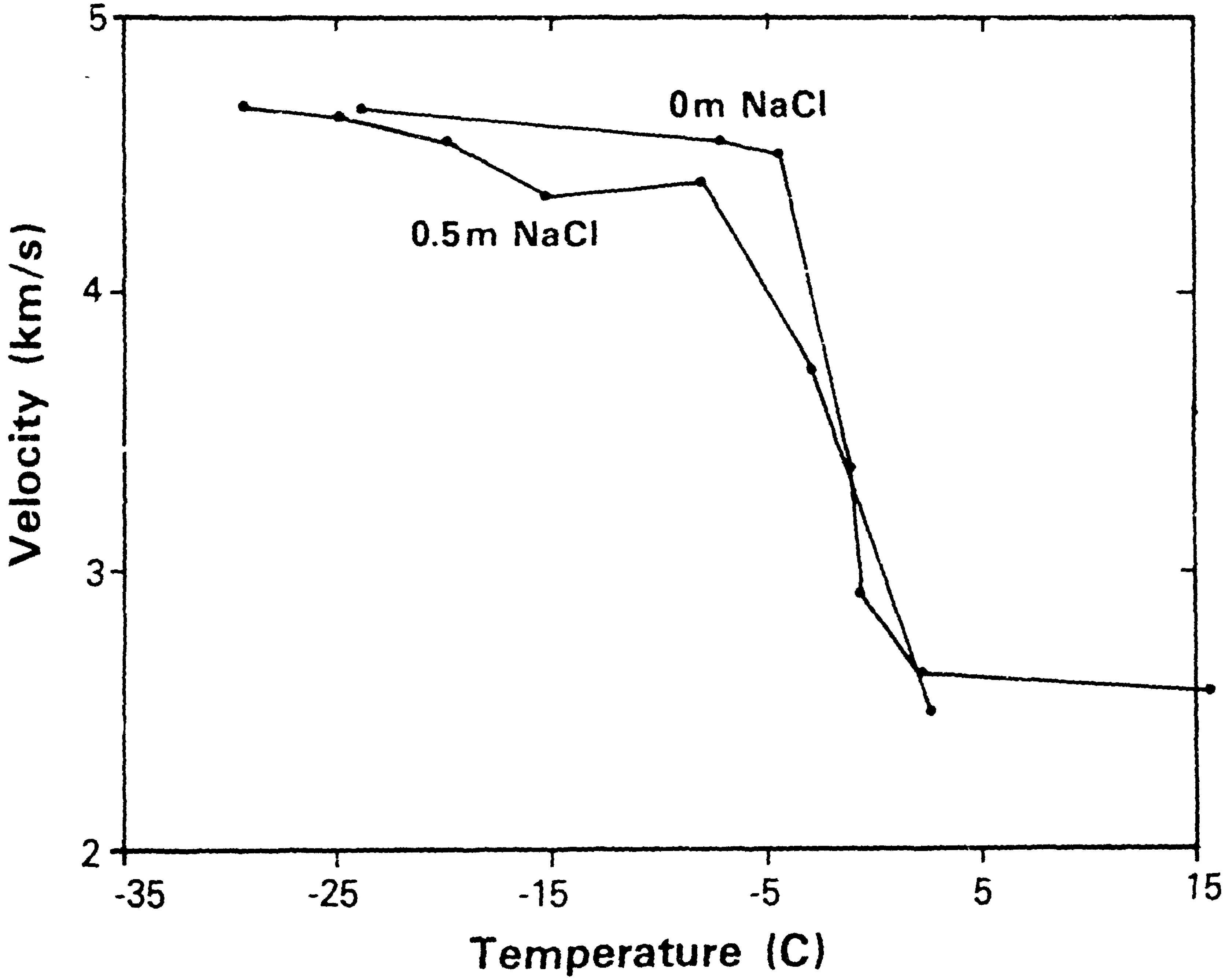

1000
100
10
1
0.1
.01
Relative Permittivity
0.5m NaCl
1m NaCl
.05m NaCl
10000
1000
100
10
Resistivity (Ω m)
.05m NaCl
0.5m NaCl
1m NaCl
10
100
1000
10000
Frequency (Hz)


Relative Permittivity
10000
1000
100
10
1
0.1
0.01
-1°C
-15°C
15°C
-30°C
Resistivity (Ω-m)
10000
1000
100
10
1
-30°C
-15°C
-1°C
15°C
10
100
1000
10000
Frequency (Hz)


Relative Permittivity
10⁷
10⁶
10⁵
10⁴
10³
10²
10
-30
-20
-10
0
10
20
30


(Resistivity (Ω -m)
10⁴
10³
10²
10
1
30
20
-10
0
10
20
30


10000
1000
100
10
1
.1
Permittivity
10
100
1000
10000
Frequency hz


0m NaCl
0.5m NaCl
Velocity (km/s)
5
4
3
2
-35
-25
-15
-5
5
15
Temperature (C)