

Dielectric study of plasticization and antiplasticization effects in Cretaceous samples from Eastern and Western Venezuela

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In this work we have studied plasticization and antiplasticization effects using the thermal stimulated depolarization current (TSDC) technique in rocks samples from Cretaceous strata located in North-Eastern (group A) and South-Western (group B) Venezuela. Drying and rehydration treatments show that the dielectric relaxation peaks of both groups are associated with the physisorbed moisture trapped at different sites in the material. In the samples from group A, drying treatments shift the peaks to higher temperatures. Rehydration treatments move the peaks towards lower temperatures and increase the intensity of the peaks. This could be explained in terms of water molecules acting as a plasticizer, that hint the molecular reorientation by increasing the free volume. Concerning the temperature shifting of the peaks the opposite behavior is observed in samples from group B. This antiplasticization effect could be explained in terms of dynamic interactions and restrictions between the sorbed water molecules and the complex polarizable entities of the material.

Keywords: Structural relaxation; TSDC; plasticization; antiplasticization.

Se presenta en este trabajo un estudio de efectos de antiplastificación y plastificación usando corrientes de depolarización estimuladas térmicamente (TSDC) en muestras de rocas de estratos Cretácicos localizados en el Noreste (grupo A) y Sureste (grupo B) de Venezuela. Tratamientos de secado y rehidratación indican que los picos de relajación dieléctrica de ambos grupos están asociados a moléculas de agua atrapadas en sitios distintos en el material. En las muestras del grupo A, los tratamientos de secado desplazan los picos hacia altas temperaturas. Los tratamientos de rehidratación los mueven hacia bajas temperaturas, aumentando su intensidad. Esto puede explicarse en términos de moléculas de agua actuando como un plastificador, que facilitan la reorientación molecular aumentando el volumen libre. Con relación al desplazamiento de los picos en temperatura el efecto contrario es observado en muestras del grupo B. Este efecto antiplastificador podría explicarse en términos de interacciones dinámicas y restricciones entre las moléculas de agua absorbidas y las complejas entidades polarizables del material.

Descriptores: Relajación estructural; TSDC; plastificación; antiplastificación.

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1. Introduction

Water molecules may act as a plasticizer or an antiplastizer. A plasticizer increases the material flexibility and processibility by increasing the free volume or reducing the H-bonding between the molecules [1]. An antiplastizer has the opposite effect, increasing brittleness and modulus by slowing down the relaxations [2]. The role of additives depends on their size, shape, polarity, and concentration, but the detailed mechanism of plasticization and antiplasticization is still a topic for research [3]. In this work we study these effects in rock samples from Cretaceous strata from at North-Eastern (group A) and South-Western (group B) Venezuela, using the thermal stimulated depolarization current technique (TSDC) [4]. Group A samples were collected near a contact identified in the field as that between Chimana (CH) and Querecual formations (QC). At the sampling locality Chimana sediments are mainly composed of thick layers of sandstone and siltstone that gradually shift to the micritic limestone characteristic of the Querecual formation. Group B samples belong to the Guayacán member (western equivalent of chimana formation). Our petrographic analyses reveal that

the Guayacán rocks are silty limestones with muscovite and residual hydrocarbon showing microstructures subparallel to the strata. These silty limestones also show pressure dissolution structures (stylolites) that are the result of low temperature ductile deformation. All through the growing of the sedimentary column, pressure increases accordingly and, in some specific locations within the sequence, part of the detritus could suffer surface dissolution into the interstitial water by mass transfer diffusional mechanisms. The dissolved material (*e.g.* calcite) could either precipitate as veins, or as the cement of the sedimentary rock, or it can even be transported away by residual liquids. Arrangements of fractures along which there has been little or no movement (joins) can act as a network of pathways or traps for fluids in the subsurfaces. Thus, an examination of their mechanical properties will influence the prospecting and prediction of hydrocarbon reservoirs. Since tectonic stylolites are commonly associated with joins, this preliminary research, focused on the study of their brittleness and/or ductile behavior via dielectric relaxation measurements, is a stepping stone into the understanding of the sealing potential (fluid flow control) of fractured sedimentary rocks.

2. Experimental

TSDC experiments were carried out in an ultrahigh-vacuum cell where the disk-shape sample ($\sim 1 \text{ cm}^2$ area and 2 mm thick) was located between two metal electrodes. A constant electrical field was established between the electrodes at a temperature T_p , sufficiently high to allow the orientation of the different dipolar species to be studied. The polarization achieved by the application of the electrical field was frozen to liquid nitrogen temperature, to maintain the perturbed condition. The depolarization current, due to the return of the material to equilibrium, is recorded as a function of the temperature increased at a constant rate of 0.1 K/s. Drying and rehydration treatments were also performed on these samples. The samples were rehydrated in a water saturated atmosphere at room temperature and dried by progressive high-vacuum outgassing at room temperature.

3. Results and Discussion

Figure 1 shows the TSDC group A spectra. As it can be observed, the total polarization represented by the area below the curves increases as the contact is approached. In this region the structure and peaks intensity change as the environment seen by the dipolar entities responsible for these relaxations varies. The TSDC group B spectra are presented in Fig. 2. A broad band composed by at least two contributions is observed. Drying and rehydration treatments performed on one sample of group A (CH4) are presented in Fig. 3. Vacuum outgassing for 1 day diminished and shifted the peaks towards higher temperatures. Rehydration treatments increased the complexity of the spectra and shifted the peaks to lower temperatures. After vacuum drying for 26 hours, the peak structure observed is similar to that of the dried state.

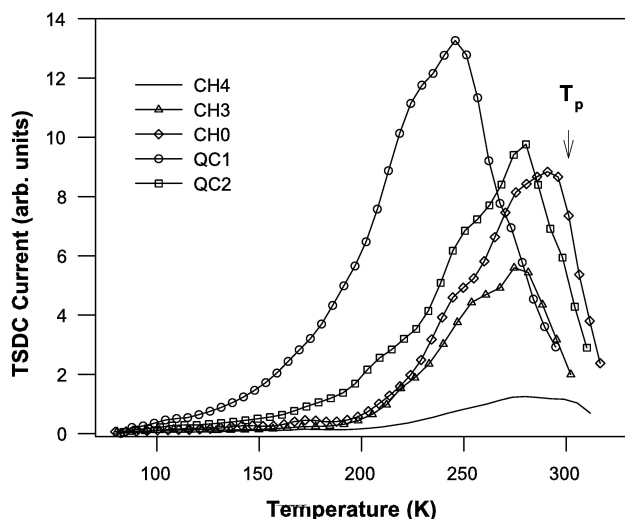


FIGURE 1. TSDC group A spectra, the nearest samples to the lithological contact are CH0 and QC1.

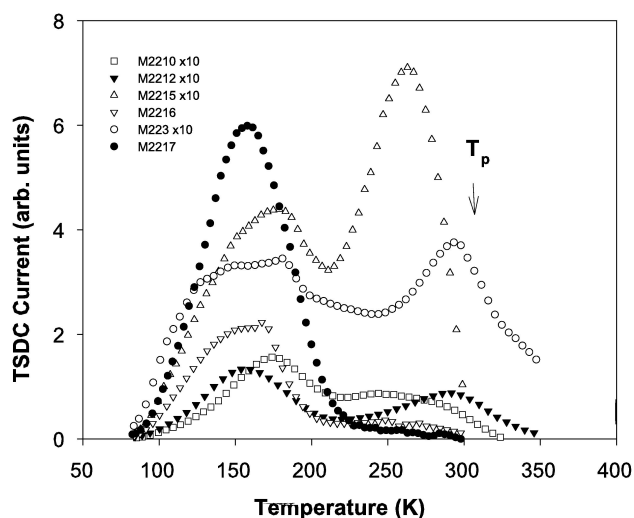


FIGURE 2. TSDC group B spectra.

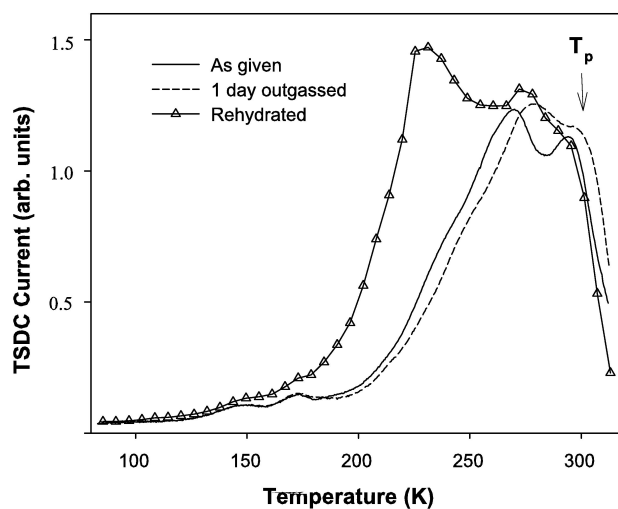


FIGURE 3. CH4 sample: Drying and rehydration treatments. 1: As given; 2: One day outgassed; 3: Rehydrated during six days at room temperature; 4: Vacuum dried for 26 hours after rehydration

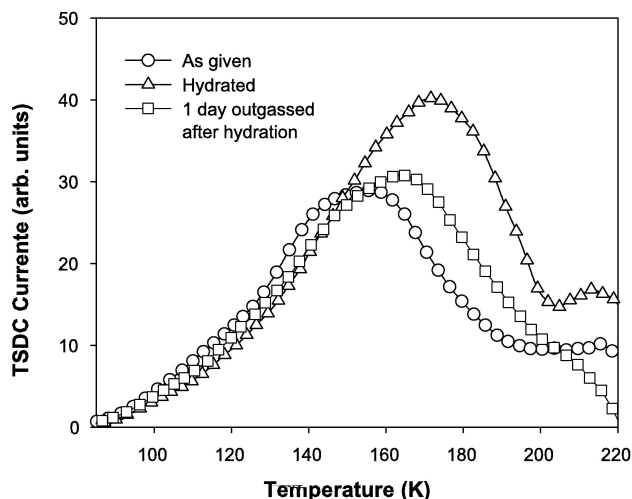


FIGURE 4. M2217 sample: Drying and hydration treatments. 1: As given; 2: Hydrated during two days at room temperature; 3: one day outgassed

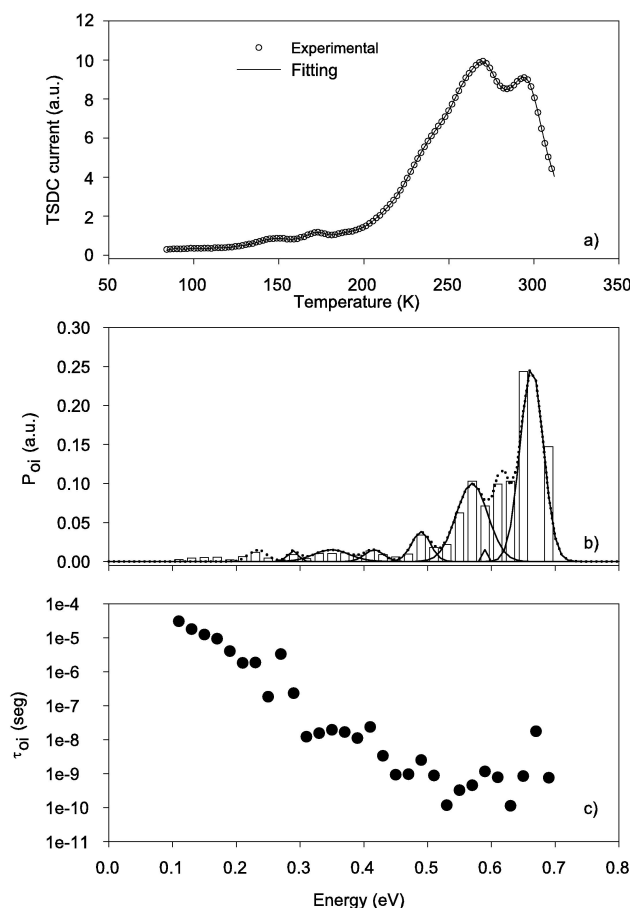


FIGURE 5. DSA analysis of CH4 sample. a) Experimental and fitted curves; b) Energy histogram of the contribution to the polarization of each elementary process; c) τ_{oi} for each adjusted elementary process

The TSDC curves of the as given, hydrated after 2 days and vacuum outgassed for 1 day after hydration of one sample of group B (M2217) are shown in Fig. 4.

Hydration and drying treatments produce the opposite effects in this sample, *i.e.*, a shift toward higher and lower temperatures respectively. The results obtained for the CH4 sample have been previously observed in casein protein [5] and poly (ethylene oxide) samples [6]. This kind of behavior was explained in terms of water molecules acting as a plasticizer that increase the free volume facilitating the molecular motion and thus displacing the peaks towards lower temperatures. On the other hand, the coupling model developed by Ngai *et al.* [7] and Xiao *et al.* [8] interprets relaxation behavior in terms of dynamics and constraints on dynamics. If water clusters added to the sample are less mobile than these originally present in the material, then the coupling motion

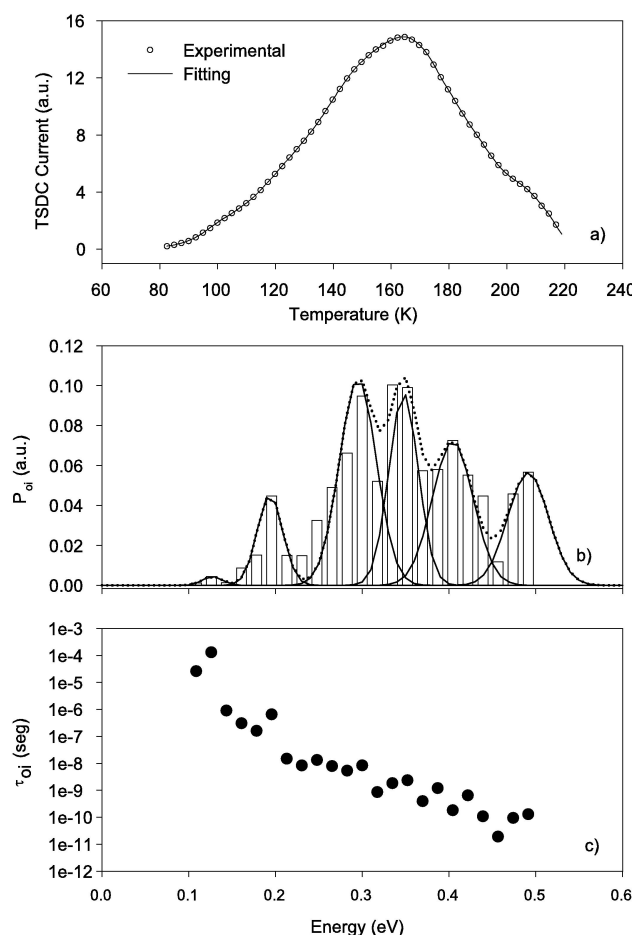


FIGURE 6. DSA analysis of M2217 sample. a) Experimental and fitted curves; b) Energy histogram of the contribution to the polarization of each elementary process; c) τ_{oi} for each adjusted elementary process.

between these two entities leads to an increase in the mean relaxation time and thus antiplasticization.

The Direct Signal Analysis (DSA) [9] was used to decompose the broad spectra into their main relaxations (see Fig. 5 and 6). The obtained relaxation times are lower for the samples from group B. Assuming that the relaxation times of the primitive moisture clusters are between these two values, the obtained results could be explained. As the range of relaxation times of the mean elementary processes of group B samples are shifted towards lower values than those from group A samples, an antiplasticization effect could be expected in the first case, while plasticization should take place in the last case. These results suggest that one of the byproducts of low temperature ductile deformation, resulting from pressure dissolution in a sedimentary sequence, could be a local increase of brittleness in the stilolites themselves.

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