

# Dielectric Behaviour of Ice Microcrystals Dispersed within Suspensions: A DTC Study

P. Pissis, L. Apekis, C. Christodoulides, and G. Boudouris  
National Technical University, Physics Laboratory A, Athens, Greece

Z. Naturforsch. **37a**, 1000–1004 (1982); received March 8, 1982

The dielectric properties of water-in-oil (W/O) suspensions have been studied by means of the depolarization thermocurrent (DTC) method in the temperature range of 85–250 K. Two predominant peaks have been observed at about 140 and 225 K. Evidence has been obtained that the peak at 140 K and the dielectric absorption observed by many investigators at sub-zero temperatures in the kHz frequency range are due to the same relaxation mechanism.

## 1. Introduction

Dielectric measurements in water-in-oil (W/O) emulsions have been carried out by many investigators using alternating current methods. These emulsions exhibit at room temperatures (20 °C–30 °C) remarkable dielectric relaxation of the Cole-Cole type in the kHz frequency range [1–3]. The experimental results are in very good quantitative agreement with Hanai's theory of interfacial polarization [1]. By a numerical analysis of Hanai's formula for the complex permittivity of the emulsion [1], Clausse [4] showed that the observed dielectric relaxation is due to conduction absorption of the dispersed water phase. (Activation energy equal to 0.22 eV, the activation energy of conductivity of water).

At sub-zero temperatures, when the dispersed phase is ice instead of water, there is no general agreement in either the experimental results reported or the theoretical interpretations. At temperatures lower than –20 °C, a dielectric relaxation of the Cole-Cole type has been observed in the kHz frequency range [5–9]. This relaxation has been related to protonic conduction [5] and to dipolar absorption in ice [8–10]. The reported experimental values for the activation energy vary over a wide range. Also, the experimental values for the limiting permittivity at low frequencies do not fit Hanai's equation (9). The properties of this relaxation have been found to change in the course of time [6, 8]. This evolution has been attributed to a solid-solid transformation connected with the existence of a microstructure of ice [11]. At temperatures be-

tween 0 °C and –20 °C an additional dielectric relaxation, located in the lower frequency range, has been observed [6, 8, 9] and related to structural changes occurring within the lattice of ice as the temperature approaches its melting point.

It is evident that further study of the dielectric properties of W/O suspensions at sub-zero temperatures is needed. This work deals with depolarization thermocurrents (DTC) measurements in W/O suspensions in the range of 85–250 K. To our knowledge this is the first time that DTC measurements on suspensions are reported. By making use of some advantages offered by the DTC method we aim to investigate the dielectric properties of W/O suspensions over a wide range of temperatures and so contribute to the understanding of the dielectric behaviour of dispersed systems at the molecular level.

## 2. Experimental

The principle of the DTC method is relatively simple [12]: The sample is polarized by an applied electric field  $E_p$  at a temperature  $T_p$ . This polarization is subsequently frozen in by cooling the sample down to a temperature  $T_0$  sufficiently low to prevent depolarization by thermal energy. The field is then switched off and the sample is warmed up at a constant rate  $b$  while the depolarization current is detected by an electrometer. In the case of a single relaxation process obeying the Arrhenius equation

$$\tau(T) = \tau_0 \exp(W/kT), \quad (1)$$

the depolarization current density  $J(T)$  is given by

$$J(T) = \frac{p_0}{\tau_0} \exp(-W/kT) \cdot \exp\left[-\frac{1}{b\tau_0} \int_{T_0}^T \exp(-W/kT') dT'\right], \quad (2)$$

Reprint requests to Dr. P. Pissis, National Technical University, Physics Laboratory A, Zografou Campus, Athens 624, Greece.

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where  $\tau$  is the relaxation time,  $W$  the activation energy of the relaxation,  $\tau_0$  the pre-exponential factor, and  $p_0$  the initial polarization.  $W$  is obtained by plotting  $\ln J$  against  $1/T$  or, more precisely, by plotting  $\ln \{P(T)/J(T)\}$  against  $1/T$ .  $\tau_0$  is then obtained from the equation

$$\tau_0 = \frac{k T_M^2}{b W} \exp(-W/k T_M), \quad (3)$$

where  $T_M$  is the temperature of the depolarization current maximum. The contribution of a DTC peak  $\Delta\epsilon$  to the static permittivity  $\epsilon_s$  is obtained from the equation

$$\Delta\epsilon = \frac{Q}{A \epsilon_0 E_p}, \quad (4)$$

where  $A$  is the cross-sectional area of the sample,  $\epsilon_0$  the permittivity of free space and  $Q$  the de-

polarization change obtained from the area under the DTC peak [13].

We used a common experimental apparatus for DTC measurements. The measuring capacitor was made of brass. The electrodes were gold foils in contact with the capacitor plates. The suspensions used are characterized by two parameters: the volume fraction  $\Phi$  of the dispersed phase (water) and the ratio  $\rho = V_e/(V_e + V_0)$ , related to the composition of the emulsion medium, in which  $V_e$  is the volume of the emulsifier (mainly zinc lanolate) and  $V_0$  the volume of the oil phase (vaseline oil). The emulsions were supplied by l'Oréal (France).

### 3. Results

In Fig. 1 the DTC is plotted against temperature in the range of 85–250 K for the suspension with  $\Phi = 0.50$ . The plot shows two predominant peaks at 136 and 227 K. For comparison we plotted in the

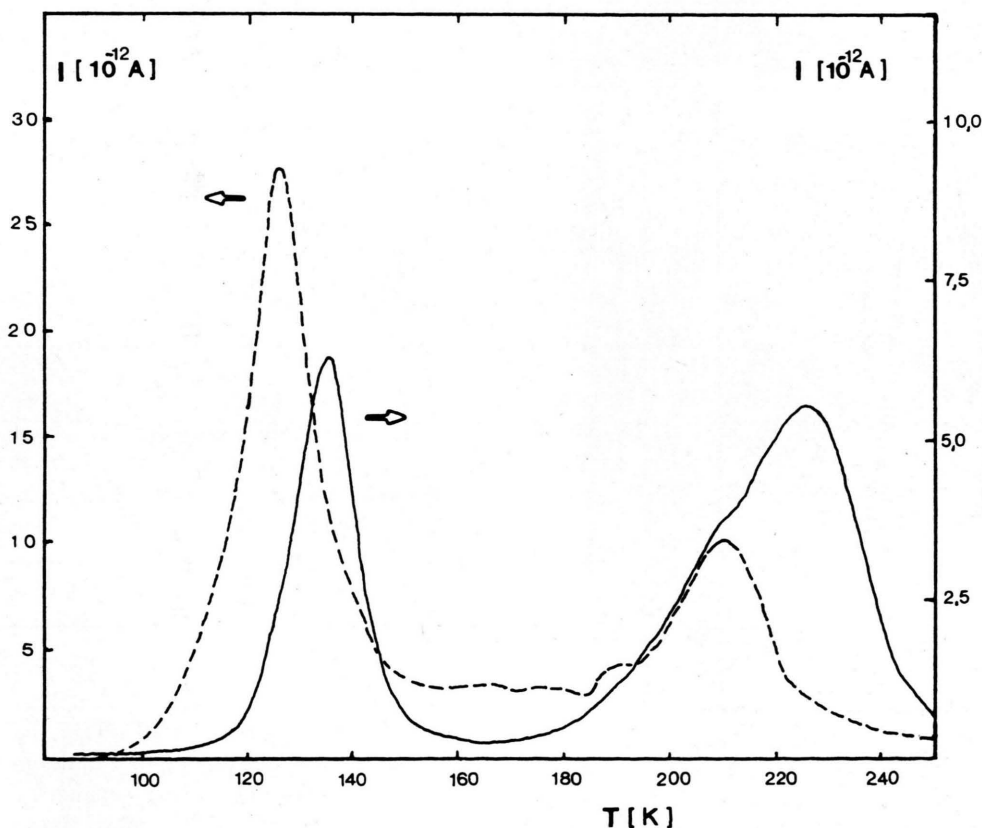


Fig. 1. DTC plots for the suspension with  $\Phi = 0.50$  (—) and a pure ice sample (----) measured with gold electrodes. The volume of the suspension was 22  $\mu\text{l}$ , the polarization temperature 230 K, the polarization time 5 min, the polarizing field 3.85 kV/cm, the heating rate 3.4 K/min. The corresponding values for the pure ice sample were 25  $\mu\text{l}$ , 243 K, 5 min, 2.60 kV/cm, 3.4 K/min.

Table 1. The characteristics of the low-temperature DTC peak in W/O suspensions in terms of the volume fraction  $\Phi$  of the dispersed phase.

$\Phi$	$\varrho$	$T_M(K)$	$W(eV)$	$\tau_0(s)$	$\Delta\varepsilon$
0.40	0.36	140 $\pm 1$	0.30 $\pm 0.02$	$1 \times 10^{-9}$	6.1 $\pm 0.6$
0.50	0.36	134 $\pm 1$	0.28 $\pm 0.02$	$1 \times 10^{-9}$	11.9 $\pm 0.8$
0.65	0.36	144 $\pm 1$	0.31 $\pm 0.02$	$1 \times 10^{-9}$	14.1 $\pm 0.9$

same figure the DTC for a pure ice sample. Our interest will be focused on the low-temperature DTC peak (peak at 136 K). The characteristics of this peak are listed in Table 1. The values in Table 1 are mean values of several measurements made on different samples from the same parent sample. The peak is satisfactorily described by (2) (Figure 2).

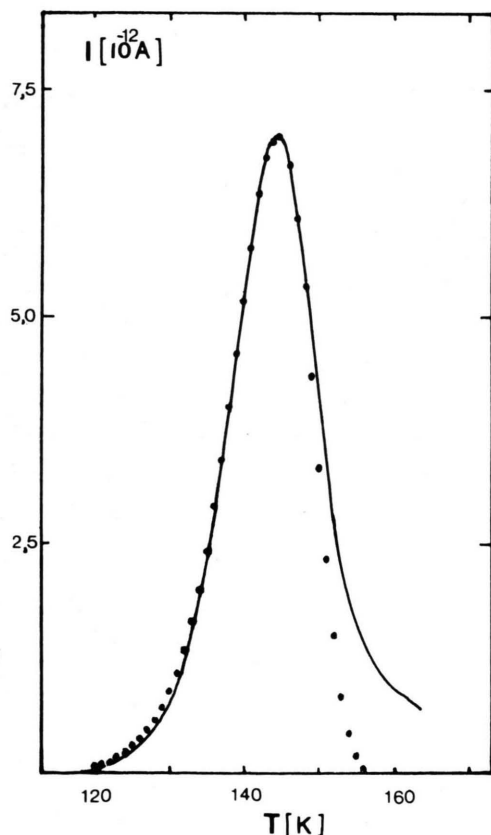


Fig. 2. Comparison of the measured (—) and calculated (.....) (with  $W = 0.33$  eV and  $\tau_0 = 3.0 \times 10^{-10}$  sec) low-temperature DTC peak in a suspension with  $\Phi = 0.65$ . The volume of the suspension was  $22 \mu\text{l}$ , the polarization temperature 155 K, the polarization time 5 min, the polarizing field 4.48 kV/cm, the heating rate 3.4 K/min.

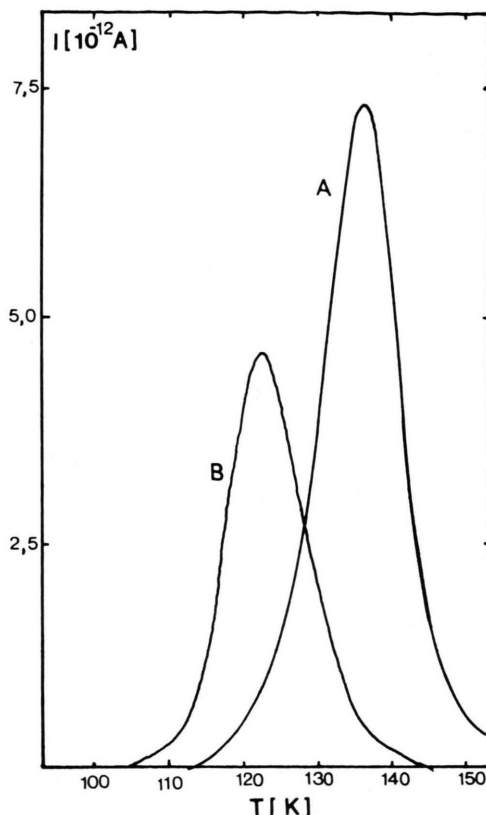


Fig. 3. Evolution with time of the low-temperature DTC peak in a suspension with  $\Phi = 0.50$ . The volume of the suspension was  $22 \mu\text{l}$ , the polarization temperature 155 K, the polarization time 5 min, the polarizing field 5.36 kV/cm, the heating rate 3.5 K/min. A: the sample was cooled down to 155 K immediately after freezing. B: after freezing the sample was preserved at 269 K for 35 minutes.

The characteristics of the peak have been found to change with time when after freezing (at about 235 K) the suspension was preserved at a constant temperature between 253 and 273 K [6, 8]. An example is shown in Figure 3. No evolution in time occurred in the samples mentioned in Table 1, since the samples were cooled down to the polarization temperature  $T_p = 155$  K immediately after freezing.

#### 4. Discussion

It is essential for the interpretation of DTC measurements to know that the sample does not undergo any structural changes during cooling or heating between the polarization temperature  $T_p$  and the temperature  $T_0$  down to which the sample is cooled. The fact that our results were independent of the cooling rate from the temperature  $T_p$  (230–220 K)

to the temperature  $T_0$  (77 K) and that they were the same after several cooling/heating cycles between  $T_p$  and  $T_0$ , provided some evidence that such structural changes did not occur in our suspensions. The results of ac measurements at temperatures down to 123 K [9] support this suggestion. Thus the use of the DTC method is justified for the dielectric study of W/O suspensions at sub-zero temperatures.

The low-temperature DTC peak in W/O suspensions seems to have the same characteristics as the dielectric relaxation observed by many investigators [5–9] using ac methods. (This is very interesting when the dielectric behaviour of W/O suspensions is compared with that of macroscopic pure and doped ice, see below.) Using the values  $W = 0.34$  eV and  $\tau_0 \approx 10^{-11}$  sec given by Chapman [5] and the experimental fact that the relaxation time  $\tau$  at the peak temperature  $T_M$  is in the range of 10–100 sec at heating rates of a few K/min, we obtain from the Arrhenius equation  $T_M = 132$ – $143$  K in very good agreement with our experimental results. Also our experimental value of  $\Delta\epsilon = 6.1 \pm 0.6$  for the suspension characterized by  $\Phi = 0.40$  and  $\rho = 0.36$  is in good agreement with  $\Delta\epsilon = 6.8$  for  $\Phi = 0.38$ ,  $\rho \approx \frac{1}{4}$  [9] and  $\Delta\epsilon \approx 8$  for  $\Phi = 0.38$ ,  $\rho \approx \frac{1}{10}$  [8], bearing in mind that  $\Delta\epsilon$  has been found to increase slightly as  $\rho$  decreases [8].

$T_M$  and  $\Delta\epsilon$  in Table 1 depend on  $\Phi$ . From Wagner's theory, valid at lower concentrations of the dispersed phase [1], Hanai's measurements in concentrated W/O emulsions at 298 K [3], and ac measurements in W/O suspensions at sub-zero temperatures [5, 8, 9] it is expected that  $T_M$  increases with increasing  $\Phi$ . Our result for the suspensions with  $\Phi = 0.50$  is not consistent with this expectation. Measurements covering a wider range of  $\Phi$  are needed to investigate the dependence of  $T_M$  on  $\Phi$ .

Under the assumption that only the low-temperature DTC peak contributes to the limiting permittivity at low frequencies  $\epsilon_1$  ( $\epsilon_1 = \Delta\epsilon + \epsilon_\infty$ , where  $\epsilon_\infty$  is the limiting permittivity at high frequencies), we obtain from the values of  $\Delta\epsilon$  listed in Table 1 and  $\epsilon_\infty = 2.5$  [8]:

$$\begin{aligned}\epsilon_1 &= 8.6 \pm 0.6 \quad (\Phi = 0.40), \\ \epsilon_1 &= 14.4 \pm 0.8 \quad (\Phi = 0.50), \quad \text{and} \\ \epsilon_1 &= 16.6 \pm 0.9 \quad (\Phi = 0.65).\end{aligned}$$

These experimental values are, in agreement with

ac measurements [8, 9], lower than the theoretical values given by the equation

$$\epsilon_1 = \epsilon_2 \frac{1}{(1 - \Phi)^3}, \quad (5)$$

where  $\epsilon_2$  is the static permittivity of the continuous phase ( $= 2.4$  [9]). The discrepancy increases with increasing  $\Phi$ . The activation energy  $W$  is, within the limits of experimental errors, independent of  $\Phi$ . Our values are close to the value of  $W = 0.34$  eV reported by Chapman [5], while they are significantly lower than the value  $W = 0.5$  eV reported by Boned *et al.* [9].

The temperature dependence of the dielectric relaxation in W/O suspensions is different from that of pure ice. The activation energy of the low-temperature DTC peak in our W/O suspensions,  $W = 0.30$  eV is close to the value of  $W = 0.34$  eV obtained by Chapman [5] from ac measurements in W/O suspensions at temperatures higher than  $-45^\circ\text{C}$ . On the other hand, by means of ac measurements the activation energy of the dielectric relaxation in pure ice has been found to be 0.62 eV at temperatures higher than about  $-50^\circ\text{C}$  and 0.28 eV at lower temperatures [14]. The value of 0.28 eV is close to the value of 0.25 eV obtained from depolarization thermocurrent measurements for the activation energy of the low temperature DTC peak (at about 125 K) in pure ice [15]. The following explanation can be given for the observed shift to a lower activation energy in pure ice at low temperatures [16]: Water molecules in pure ice are reoriented by the diffusion of Bjerrum D- and L-defects. The activation energy of the dielectric relaxation of 0.62 eV at high temperatures is due to the production and motion of intrinsically generated D- and L-defects. The shift to a lower activation energies at lower temperatures is caused by the decrease in the concentration of intrinsically generated D- and L-defects with decreasing temperature, so that D- and L-defects generated by physical or chemical impurities become dominant. The impurity-generated D- and L-defects presumably have a smaller heat of formation than the intrinsically generated D- and L-defects, and may be produced in maximum numbers physically possible, in which case their heat of formation does not contribute to the activation energy. In HF-doped ice the same activation energy of 0.28 eV has been observed in the whole temperature range between  $0^\circ\text{C}$  and  $-170^\circ\text{C}$  [14]. It is

believed that this is due to the fact that the D- and L-defects generated by the HF molecules dominate over the intrinsically generated D- and L-defects in the whole temperature range.

One of the results of the present study is that the same independence of  $W$  from temperature that was observed in HF-doped ice [14], appears to exist also in W/O suspensions (0.34 eV at higher temperatures [5], 0.30 eV at low temperatures). Taking into account the interpretation of Johari and Whalley [16] for the T-dependence of  $W$  in pure ice, we conclude that this indicates that in W/O suspensions extrinsically generated D- and L-defects dominate over the intrinsically generated D- and L-defects in the whole temperature range. As for the extrinsic defects that generate D- and L-defects, we suggest that they must be physical defects whose concentration in frozen W/O suspensions is high due to supercooling breakdown. The activation energy  $W$  and the peak temperature  $T_M$  of the low-temperature DTC peak in W/O suspensions are higher than the corresponding values of the low-temperature DTC peak in pure ice. A possible explanation of this behaviour is that a higher activation energy is needed for the motion of D- and L-defects in the ice microcrystals of the W/O suspensions than in macroscopic pure ice, because of the higher concentration of physical defects in the former. However, further study is needed for this explanation to be verified.

According to our explanation of the dielectric relaxation in W/O suspensions, the dielectric behaviour of W/O suspensions resembles that of HF-doped ice in that in both cases the extrinsically generated D- and L-defects dominate over the intrinsically generated D- and L-defects in the whole

temperature range. In HF-doped ice D- and L-defects are extrinsically generated by HF molecules (extrinsic chemical impurities), while in W/O suspensions by extrinsic physical defects.

## 5. Conclusions

The main results of this work are: (a) the DTC method can be applied to W/O suspensions, (b) the DTC peak at about 140 K in W/O suspensions and the dielectric absorption observed at sub-zero temperatures in the kHz frequency range are due to the same relaxation mechanism, and (c) a possible explanation of the observed dielectric behaviour of W/O suspensions is that extrinsically generated D- and L-defects dominate over the intrinsically generated D- and L-defects in the whole temperature range, and the activation energy of the dielectric relaxation is only due to the motion of D- and L-defects.

We think that further study is needed in order to understand the dielectric behaviour of W/O suspensions at sub-zero temperatures at the molecular level. It would be particularly interesting to compare the characteristics of the low-temperature DTC peak in W/O suspensions at advanced states of evolution in time, with those of the low-temperature DTC peak in macroscopic pure ice. Experiments along these lines are now in progress in our laboratory. It would also be interesting to investigate by means of ac methods whether the activation energy of the dielectric relaxation in W/O suspensions is independent of the temperature, as found in the present work by comparing our DTC measurements at low temperatures with ac measurements by other investigators at higher temperatures.

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