A COMPARATIVE STUDY OF THE DIELECTRIC BEHAVIOUR OF ICE IN WATER-CONTAINING SYSTEMS[1]

P. PISSIS, L. APEKIS and C. CHRISTODOULIDES

*National Technical University of Athens, Physics Department,
Zografou Campus, GR-157 73 Athens, Greece*

Résumé.- La relaxation diélectrique dipolaire de la glace dans des systèmes conte-
nant de l'eau a été étudiée par la méthode des thermocourants de dépolarisation
(T.C.D.). Ces systèmes sont: glace polycristalline pure, émulsions du type eau-dans-
huile et du type huile-dans-eau gelées, solutions aqueuses de saccharides gelées,
échantillons solides hydratés de saccharides, d'acides aminés et de protéines et
feuilles de plantes. On a trouvé que les paramètres de relaxation diffèrent de façon
caractéristique pour les différents systèmes étudiés. Les résultats expérimentaux
sont discutés en termes de concentration de défauts d'origine physique dans les sys-
tèmes de la glace et de différents modes de liaison de l'eau dans les matériaux hy-
dratés. Pour caractériser l'état physique de l'eau dans les systèmes la contenant,
la méthode T.C.D. s'est montrée un outil très efficace.

Abstract.- The dipolar dielectric relaxation of ice in several water-containing sy-
stems has been studied by means of the thermally stimulated depolarisation (TSD) me-
thod. These systems are: pure polycrystalline ice, frozen water-in-oil and oil-in-
water emulsions, frozen aqueous solutions of saccharides, hydrated solid samples of
saccharides, aminoacids and proteins and plant leaves. The parameters describing the
relaxation are in a characteristic way different for different systems. The results
are discussed in terms of the concentration of physical defects in the ice systems and
the different binding modes of water in hydrated materials. The TSD method proves
itself a powerful tool in characterizing the neighbourhood of reorientating water mo-
lecules in water-containing systems.

1. Introduction

We report in this paper on the dielectric behaviour of ice in several water-contai-
ning systems studied by means of the thermally stimulated depolarisation (TSD)
technique. These systems are: pure polycrystalline ice, frozen W/O and O/W
emulsions, frozen aqueous solutions of saccharides, hydrated solid samples of saccha-
rides and proteins and plant leaves.
    The paper has two objectives. The first is to contribute to a better under-
standing of the dielectric properties of ice. We think that experiments on different
ice systems can be very useful in checking the theories on the electrical and die-
lectric properties of ice. The second objective is related to the development in re-
cent years of dielectric techniques into a powerful tool for the study of the binding
modes of water in hydrated materials (irrotationally bound water, loosely bound wa-
ter, free water [1,2]). Their use is based on the strong dipolar character of the
water molecule and the dependence of the microdynamics of its reorientation in an ap-
plied electric field on its neighbourhood. The characteristics of the dielectric re-
laxation which is attributed to reorientation of sorbed water molecules can then be

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expected to be different than those in macroscopic pure water or ice and different for different binding modes. In fact, the spectrum of dielectric relaxation times of sorbed water molecules is usually both at temperatures above and below 0° C significantly more complex than that of macroscopic water or ice and is also shifted to larger times. However, just because of this complexity, the interpretation of the results of dielectric measurements in hydrated materials in terms of different binding modes of water molecules is still controversial and very often similar experimental results have been interpreted in quite different ways [3]. By studying the characteristics of the dielectric relaxation due to reorientation of water molecules in macroscopic ice and in ice in several water-containing systems we hope to contribute to the clarification of this problem.

2. Experimental.

The TSD method is as follows [4]. The sample is polarised by an applied electric field E_p. This polarisation is subsequently frozen in by cooling the sample down to a temperature T_0 sufficiently low to prevent depolarisation by thermal energy. The field is then switched off and the sample is warmed up at a constant rate b, while the depolarisation current, as the dipoles relax, is detected by an electrometer. Thus for each polarisation mechanism an inherent current peak can be detected. A major feature of the TSD method, which makes it attractive for our purposes, is that it offers the possibility to experimentally resolve relaxation processes arising from sets of dipoles with slightly different relaxation times.

In the case of a single relaxation process obeying the Arrhenius equation

$$\tau(T) = \tau_0 \exp(W/kT) \tag{1}$$

the depolarisation current density J(T) is given by the equation

$$J(T) = \frac{P_0}{\tau_0} \exp(-W/kT) \exp\left[-\frac{1}{b\tau_0} \int_{T_0}^{T} \exp(-W/kT')\, dT'\right] \tag{2}$$

where τ is the relaxation time, W the activation energy of the relaxation, τ_0 the pre-exponential factor, T the absolute temperature, k Boltzmann's constant, and P_0 the initial polarisation. The analysis of the shape of this curve makes it possible to obtain the activation energy W, the pre-exponential factor τ_0, and the contribution $\Delta\varepsilon$ of a peak to the static permittivity [3-5].

We used a cryostat for measurements in the temperature range 77-300 K. Details of the experimental apparatus and the preparation of the samples have been given in previous publications [6-11].

3. Results and Discussion.

TSD measurements on macroscopic polycrystalline pure ice show two predominant peaks at about 120 and 220 K. The low-temperature TSD peak at about 120 K has been attributed to the reorientation of water molecules in ice [6] and the high-temperature peak at about 220 K to space charge relaxation [12]. Since we are interested in the dipolar dielectric relaxation of water molecules, we confined our studies to the low-temperature range of 77-170 K. Figure 1 shows the peak at 120 K. Detailed experimental studies reported at this Conference by Dr. Apekis show that the peak is not single. The main relaxation mechanism contributing to it is characterized by a narrow continuous distribution of relaxation times around a mean value. The mean value of the activation energy is in the range of 0.25-0.30 eV, depending on the method of evaluation. The results of TSD measurements on macroscopic polycrystalline pure ice have been explained at the molecular level by extending Jaccard and Gränicher's theory of the dielectric properties of ice [13] to low-temperature TSD measurements [14]. In this extension the reorientation of water molecules is realized by the motion of Bjerrum D and L defects.

In all the systems studied a TSD band was observed in the temprature range 77-170 K. The position, the shape and the magnitude of the band as well as the dependence of these quantities on the water content are in a characteristic way different for different systems. Our measurements provided several indications supporting the hypothesis that the band is due to reorientation of water molecules:

i) The depolarisation charge obtained from the area under the TSD band was found to increase for the same system with increasing water content. In the case of hydrated compressed pellets of saccharides and proteins the low-temperature TSD band appears only for water contents h higher than a critical hydration level h_c, which is different for different materials. For h larger than h_c the depolarisation charge increases linearly with increasing h (Fig.2). In the case of frozen water-in-oil e-mulsions the increase of the depolarisation charge with increasing water content is not linear for reason we can well understand [15].

ii) The position and the shape of the band were found to be, for the same sys-tem and the same water content, independent of the polarising field, while the depo-larisation charge was found to increase linearly with increasing polarising field. An example is shown in figure 3. These results indicate that the band is due to dipolar rather than space charge relaxation [5], in consistency with the hypothesis that the reorientation of water molecules is its cause.

iii) We prepared and studied in some cases systems with H_2O being replaced by D_2O. For each system, and for the same water content, the low-temperature TSD bands in the H_2O- and D_2O- systems were similar in shape, the band in the D_2O- system being shifted by 4 K towards higher temperatures. Also in pure H_2O and D_2O ice the low-temperature TSD peaks are similar in shape, the peak temperature T_M being 4 K higher in heavy ice. An example is shown in figure 4.

Regarding the shape of the low-temperature TSD band, three different types of behaviour have been observed. Type S is that of an approximately single peak (to the same degree as that in macroscopic polycrystalline pure ice). Frozen water-in-oil e-mulsions and frozen concentrated solutions ($c \gtrsim 0.7$ mol/litre) of the monosaccharides glucose, mannose and galactose show this type of behaviour. The peak temperature T_M is higher than in macroscopic polycrystalline pure ice. Type M is that of a peak which is both significantly broader and located at a higher temperature than the peak in macroscopic polycrystalline pure ice. Dilute solutions ($c \lesssim 0.7$ mol/litre) of the monosaccharides glucose, mannose and galactose, hydrated compressed pellets of the saccharides galactose and maltose monohydrate, the polysaccharide cellulose and the protein casein and plant leaves show this type of behaviour. Finally, type D is that of a double peak, the first peak being located at the same temperature as the peak in macroscopic polycrystalline pure ice and the second peak at a higher temperature. Frozen oil-in-water emulsions and frozen solutions of the saccharides arabinose, ri-bose, maltose, lactose and cellobiose show this type of behaviour.

In concentrated solutions ($c \gtrsim 0.7$ mol/litre) of the monosaccharides glucose, mannose and galactose, the temperature of the approximately single peak is about 130K and the (mean) activation energy W about 0.34 eV. We have good reasons to believe that the peak is due to the reorientation of water molecules, which are influenced by the presence of the solute molecules [3,9].

In dispersions of ice microcrystals in oil the peak temperature T_M and the mean activation energy W depend on the volume fraction Φ of the dispersed water phase. For $\Phi = 0.40$, for example, we found $T_M = 140$ K and $W \approx 0.34$ eV. The properties of the peak were found to change with time, when after freezing at T_{fr} the emulsion was preserved at a constant temperature between T_{fr} and $0^{\circ}C$ [7]. An example is shown in figure 5. A detailed study by means of peak resolving experimental techniques offered by the TSD method [9-11] shows that the peak is characterized by a continuous distribution of relaxation times with both the activation energy W and the pre-exponential factor τ_0 being distributed. It shows further that the dielectric behaviour of dispersed ice microcrystals resembles strongly in some aspects (such as the values and the tem-perature dependence of the activation energy W and the change of the dielectric pro-perties with time) that of macroscopic HF-doped ice [16] and ice samples with high concentrations of crystal inperfections [17,18]. A possible explanation of the lar-ger relaxation times and the higher activation energy in all these ice systems, as compared to macroscopic polycrystalline pure ice, is that the motion of orientational D and L defects is hampered by the high concentration of physical defects.

In dilute solutions ($c \lesssim 0.7$ mol/litre) of the monosaccharides glucose, mannose and galactose, the broad peak has been studied in detail. By varying the solute con-centration over a wide range and mainly by using several experimental techniques of-fered by the TSD method, such as the technique of varying the polarisation temperatu-re T_p, the technique of increasing the resolving power of the TSD method by lowering
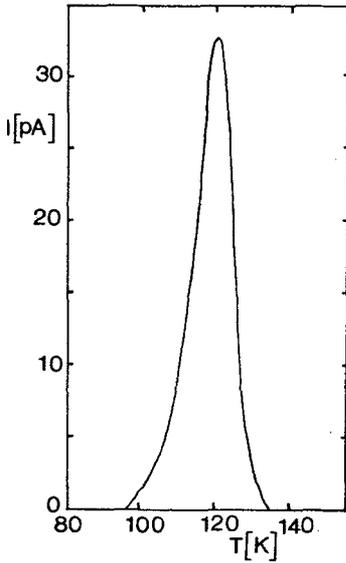
Fig.1.- The low-temperature TSD peak of
macroscopic polycrystalline pure ice.
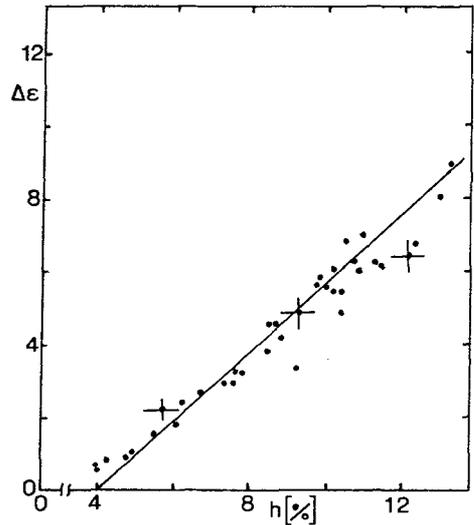
Fig.2.- Linear correlation between the
contribution $\Delta\varepsilon$ of the peak in hydrated
maltose to the static permittivity and
its water content h.
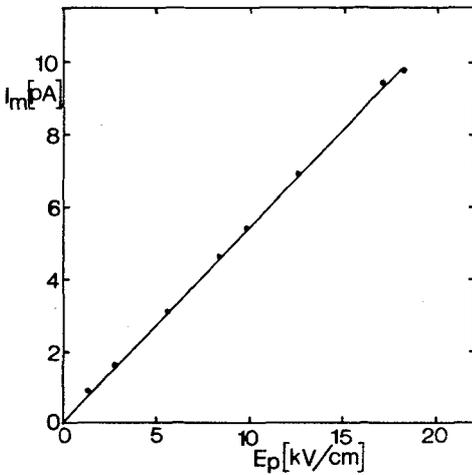
Fig.3.- Linear correlation between peak's
amplitude I_m and polarizing field E_p for
the peak of Olea europaea leaves.
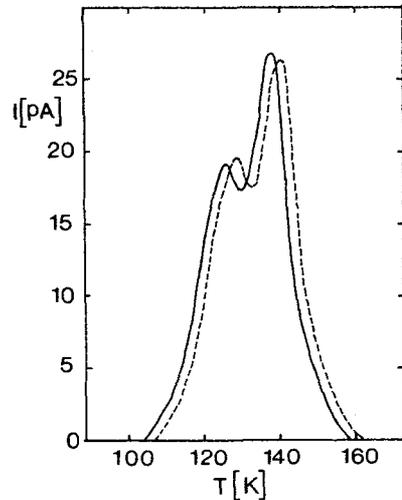
Fig.4.- TSD bands for 0.001 M maltose
solution in H_2O (——) and D_2O (---).

the heating rate b, the partial heating technique and the thermal sampling technique,
we could show that the peak is multiple and the corresponding relaxation process con-
tinuously distributed, with both the activation energy W and the pre-exponential fa-

ctor τ_0 being distributed parameters. A linear ralationship exists between W and $\ln\tau_0$, the so-called compensation law (Fig.6). The results show that in these solutions there is a continuous transition from hydration to free water molecules. On the base of the specific hydration model [19] this results from the fact that glucose, mannose and galactose can fit well into the ice structure.

The results in hydrated compressed pellets of galactose, maltose, cellulose and casein make it reasonable to accept that the broad peak, which appears only for water contents h higher than a critical hydration level and then increases linearly with increasing h, is due to the reorientation of loosely bound water molecules. The critical hydration level corresponds to the fraction of water molecules that are tigthly (irrotationally) bound. Its evaluation is useful in checking models predicting the number of hydration sites in the molecular structure. The results show that the peak is characterized by a continuous distribution of relaxation times with the activation energy W being a distributed parameter (Fig.7). The mean values of τ and W are (slightly) different for different systems and different water contents but always higher than the corresponding values for macroscopic polycrystalline pure ice. The results may be explained by the hypothesis of the existence of a variety of structures of modified water. An alternative explanation is that the continuous distribution of relaxation times arises from a distribution of sizes of water clusters.

Measurements in plant leaves show similar results to those in hydrated saccharides and proteins, with the mean values of τ and W being even higher despite their larger water contents.

The double peak in frozen oil-in-water emulsions and in frozen aqueous solutions of the saccharides arabinose, ribose, maltose, lactose and cellobiose could be experimentally resolved into two peaks (Fig.8) corresponding to two discrete kinds of water molecules, namely free and hydration molecules. These saccharides cannot fit well into the ice structre and thus act as structure breakers.
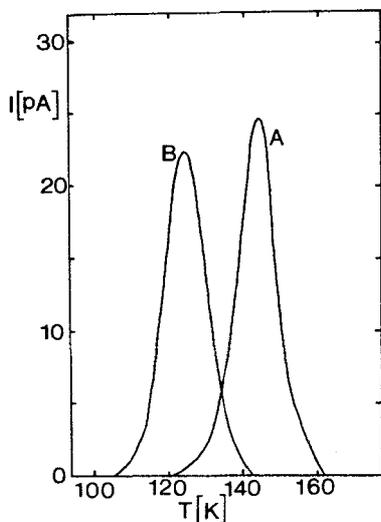
Fig.5.- Evolution with time of the TSD peak in an ice emulsion with $\Phi = 0.40$:A, immediately after freezing; B, after 1 hour preservation at -2°C.
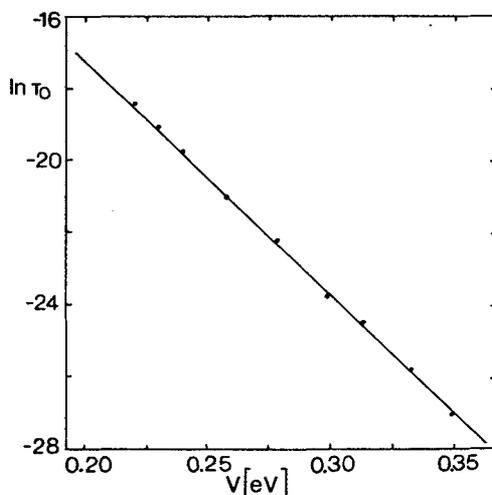
Fig.6.- Linear relationship between W and $\ln\tau_0$ of the thermal sampling responses isolated in the TSD band of the 0.1 M mannose solution.
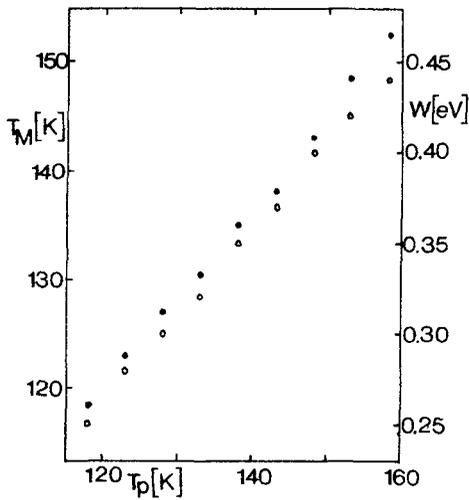
Fig.7.- Peak temperature T_m (●) and activation energy W (o) of the thermal sampling responses isolated in the TSD band of hydrated cellulose with $h = 20.4\%$ as a function of the polarisation temperature T_p.
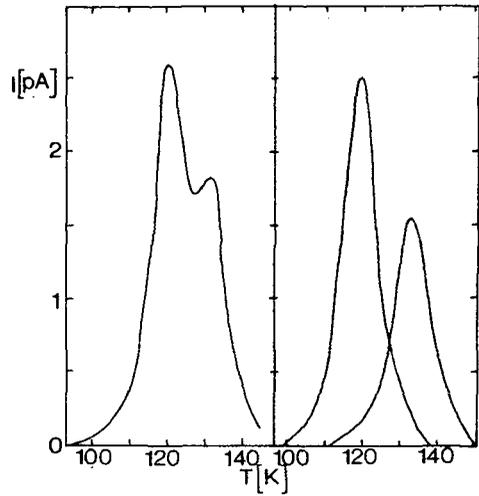
Fig.8.- Analysis of the TSD band in a frozen oil-in-water with $\Phi = 0.40$ into two discrete peaks.

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COMMENTS

T.MATSUO

In our calorimetric experiment, we found a very slow change of the property of ice sample around 100 K that took days for completion (Keda, Matsuo and Suga, J. Phys. Chem. Solids, $\underline{43}$, 1165 (1982) and references theirin). Since the TSD experiment can also detect slow changes, it should be interesting to do the TSD measurement on the ice annealed around 100 K in the electric field.

Answer :

In fact, the TSD technique is very suitable in studying slow changes of properties of materials, since it corresponds to frequencies in the range of $10^{-1} - 10^{-4}$ Hz. The TSD technique has already been used in the study of slow phase transitions in polymers and in other materials too . We intend to study the changes observed in ice by calorimetric measurements around 100 K by using the TSD technique in its usual form, as well as without the application of an electric field. We think that it is interesting to see if the application of a dc field has any influence on the observed changes.

VANDERSCHUEREN, J. and GASIOT, J., in Thermally Stimulated Relaxation in Solids, P. Bräunlich ed. (Springer Verlag, Berlin) 1979.