Biophysical Journal Volume 70 March 1996 1485-1493

Dielectric and Conductivity Studies of the Hydration Mechanisms in Plant Seeds

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ABSTRACT The hydration mechanism of various plant seeds has been investigated by a) sorption-desorption isotherms, b) ac-dielectric spectroscopy in the 10 Hz to 1 GHz frequency range and the −80 to + 40°C temperature range, and c) thermally stimulated depolarization current techniques in the −170 to +23°C temperature range. Seeds of different chemical composition were studied at water contents varying between 0 and 40% w/w (dry weight basis). Our experimental results permitted us to determine i) the diffusion constant of water in the samples, found to be between 1.4×10^{-11} and 3.7×10^{-11} m^2/s; ii) a critical water content corresponding to the completion of the primary hydration layer, which is in the range 0.11–0.17 w/w, depending on the seed nature; and iii) the activation energy of the main relaxation mechanism, found to be equal to 0.54 ± 0.05 eV. Moreover, they make it possible to investigate the dependence of various parameters (conductivity, molecular mobility, plasticizing effect of water) on the water content of the sample, to follow the crystallization of water in the seeds as a function of temperature and confirm that it is not a reversible process, to study the dehydration process as a function of temperature and time, and to propose an alternative technique for the determination of the moisture content in seeds.

INTRODUCTION

Seeds, like other biomaterials, are quite complex and heterogeneous in nature, compared to synthetically prepared engineering materials. A true understanding of the relation between their electrical and dielectric properties on the one hand and the state of their hydration water on the other is essential for at least two purposes. The first is to construct and test the validity of models for the dielectric properties of seeds as a function of their water content. Many practical applications derive from these, e.g., monitoring of water content with electrical techniques, developing or improving dielectric or microwave heating techniques used for processing of food materials in industrial and domestic applications, and developing technologies for seed storage, gene banks, and preservation of pharmaceutical products (Bruni and Leopold, 1992; Nelson, 1991; Carreri et al., 1990; Bruni and Leopold, 1991; Peleg, 1993; Ratkovič, 1987). The second aim is to use the dielectric relaxation spectroscopy for investigating and interpreting the hydration properties of seeds, in terms of free and bound or freezable and unfreezable water, and in terms of a glass transition reported in seeds (Carreri et al., 1990), the temperature of which depends very markedly on the water content (Bruni and Leopold, 1991). This glass transition seems to be directly related to the frost resistance of seeds and their ability to survive desiccation (Peleg, 1993), the glassy state preventing metabolism as well as damage caused by dehydration.

Studies of the state of water in intact seeds as well as in seed flour samples have mainly employed NMR techniques (Ratkovič, 1987; Jenner and Jones, 1990), EPR spectroscopy (Bruni and Leopold, 1991), mechanical properties measurements (Peleg, 1993; Singh et al., 1991), differential scanning calorimetry (Williams and Leopold, 1989; Vertucci, 1990), thermally stimulated depolarization currents (Nelson, 1991), dielectric relaxation spectroscopy, and conductivity measurements (Carreri and Giasanti, 1984; Holmes et al., 1991; Kraszewski and Nelson, 1989, 1993; Nelson, 1994a,b; Schafer et al., 1986; Mudgett et al., 1980; Nelson et al., 1994; Tran et al., 1984; Shegoleva, 1984).

Nondestructive techniques for the measurement of seed moisture content using microwave dielectric spectroscopy have been proposed by a number of authors (Holmes et al., 1991; Kraszewski and Nelson, 1989, 1993; Nelson, 1994a). Principles and equipment used for this purpose have been discussed and presented, especially by Nelson and Kraszewski (Kraszewski and Nelson, 1993; Nelson, 1994a), and analytical expressions for the relative permittivity and the loss factor of cereal grains as a function of bulk density, moisture content, and frequency have been developed by the same authors (Kraszewski and Nelson, 1989). Dielectric relaxation spectroscopy at the gigahertz range has also been used for investigating the state of water in seeds (Schafer et al., 1986), in granular and powdered biomaterials, as well as in dried and fresh fruits and vegetables (Nelson, 1994b; Nelson et al., 1994; Tran et al., 1984), and for determining variety differences of wheat grains (Shegoleva, 1984). A comprehensive review of the dielectric properties of agricultural products is found in Bruni and Leopold (1992).

In this work, the hydration properties of seeds were investigated with dielectric techniques in the low and intermediate frequency range in association with water sorption-desorption techniques. More specifically, the experimental techniques employed were as follows: a) equilibrium sorption isotherms at 40°C, in the 0 to 95% relative humidity

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Received for publication 7 July 1995 and in final form 2 November 1995.

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0006-3495/96/03/1485/09 $2.00

(RH) range; b) isothermal sorption-desorption kinetics at room temperature; c) thermally stimulated depolarization current (TSDC) techniques in the temperature range −170 to +23°C; and d) ac-dielectric spectroscopy in the frequency range 0.1 Hz to 1 GHz and the temperature range −80 to +40°C.

To our knowledge, this is the first time that such broad ranges of frequency (10^{-4}-10^{9} Hz) and temperature (−170°C to 40°C) have been covered in dielectric studies of seeds. These broad ranges allowed us to investigate simultaneously the molecular mobility of water molecules in seeds and the influence of water on the molecular mobility of the seed constituents at different hydration values. The dielectric spectroscopy results, combined with those obtained by equilibrium and dynamical sorption isotherms, will be discussed, using different concepts developed for hydration studies.

Seeds of different genotypes have been used: bean, wheat, lent, chick pea, white lupine, African pea. From the dielectric point of view the above seeds have been found to fall into two major classes, one comprising wheat and the other comprising bean and similar seeds. As a consequence, results reported here concern mainly bean and wheat seeds, which have been studied in more detail.

EXPERIMENTAL PROCEDURES

For the preparation of our samples the seeds were uniformly ground and the powder was compressed at a pressure of 6 tons into cylindrical pellets of 13 mm diameter and 1.5–2 mm height. The density of the dry pellets was 1.16 (±0.02) g cm^{-3}. The water content, h, defined as grams of water per gram of dry material, was varied up to about 40% by equilibrating the samples in closed jars over saturated salt solutions of known relative humidity (RH), at a temperature of 40°C. The pellets were dried at 110°C and 5×10^{-2} torr for 24 h to determine their dry weights.

Equilibrium water sorption isotherms were measured at 40 (±1)°C by allowing completely dehydrated samples to equilibrate to constant weight in closed jars in which RH was monitored and was gradually increased between 6% and 97%. Dynamic water sorption and desorption measurements, aiming at studying the kinetics of sorption, were carried out as follows. The samples were hydrated by exposure at 0.97 relative humidity or, alternatively, dehydrated in the way described above; they were then allowed to equilibrate at ambient RH at 25 (±1)°C on the pan of a Sartorius A2006 analytical balance, while their weight was automatically recorded as a function of time.

The principle of the TSDC technique, described in detail in Van Turnout (1980) and Anagnostopoulou-Konsta and Pissis (1987), is the following. The sample, positioned between the electrodes of a parallel-plate condenser, is polarized by a DC electric field at a polarization temperature, which in our case was room temperature. With the field still applied, the temperature is lowered to the temperature of liquid nitrogen (in our case) to freeze in the polarization. After the field is switched off, the sample is warmed up at a linear heating rate under short-circuit conditions, and the depolarization current, induced by the relaxation of the polarization, is detected by an electrometer. In this way, for each type of relaxation mechanism, either of dipolar or of space charge origin, a separate current peak is recorded, which can be analyzed to obtain its activation energy, the pre-exponential factor, and the contribution of the peak to the static permittivity (Vanderschueren and Gasiot, 1979). The TSDC technique corresponds thus to measuring dielectric losses as a function of temperature at fixed frequencies of 10^{-3} to 10^{-4} Hz. For a detailed description of the apparatus and the special techniques offered by the TSDC method we refer to Vanderschueren and Gasiot (1979).

Broad-band AC dielectric spectroscopy is a well-known and established technique that makes it possible to determine dielectric permittivity, dielectric loss, and conductivity as a function of the frequency of the applied field. It has been extensively applied to the investigation of the dielectric and conductivity properties of biomaterials (Pethig, 1979; Pethig and Kell, 1987; Bone and Zaba, 1992). A Hewlett-Packard HP 4292A impedance analyzer, interfaced with a Hewlett-Packard VECTRA computer and associated with an ANDO oven and sample holder, was used to measure the permittivity and loss over the frequency range 10 Hz to 13 MHz and in the temperature range −60 to +20°C and to analyze the recorded data. For measurements between 5 Hz and 1 GHz, the samples were placed in a shielded parallel-plate condenser, which was inserted into a transmission line. With a novel broadband calibration method (Pelster et al., 1994) the complex dielectric function was calculated from the measured transmission coefficient of the system. Measurements were performed with two network analyzers (5 Hz to 200 MHz, HP 3577B; 200 MHz to 2 GHz, HP 3510B/1000 frequency points).

RESULTS AND DISCUSSION

Water sorption-desorption isotherms

The equilibrium sorption isotherms (i.e., the water uptake as a function of relative humidity; not shown) exhibit the same behavior for all types of seeds studied. The shape of the plots was quite complex, probably because of the heterogeneous nature of the seeds, and could not be analyzed with the help of the standard adopted models described in the literature (Brunauer et al., 1938). More carefully and systematically measured sorption-desorption equilibrium isotherms, combined with similar measurements on isolated seed constituents, are most probably needed for any quantitative information to be gathered.

The sorption-desorption data for bean and wheat samples at 25°C are shown in Fig. 1. $(\Delta m)_t$ is the water uptake or loss at time t (sorption or desorption respectively), $(\Delta m)_\infty$ is the corresponding limiting value at equilibrium, and d is the thickness of the sample, presumed constant over the whole

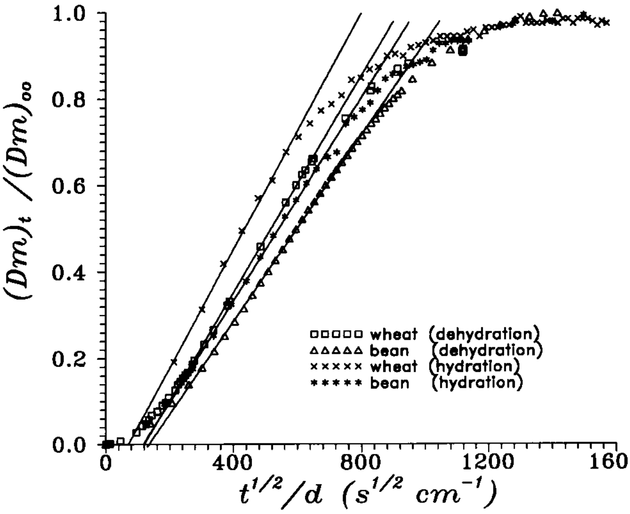

FIGURE 1 Sorption-desorption dynamics recorded with wheat flour and bean flour samples at ambient temperature and relative humidity conditions. Dm stands for Δm. The straight lines represent best fits of Eq. 1 to the initial part $[(\Delta m)_t/(\Delta m)_\infty < 0.5]$ of the corresponding curves.

process. Assuming a Fickian behavior with constant diffusion coefficient D, the following equation holds for dynamic water sorption and desorption isotherms at relatively small time values, i.e., corresponding to $(\Delta m)_t/(\Delta m)_\infty < 0.5$ (Crank, 1956):

$$(\Delta m)_t/(\Delta m)_\infty = \frac{4}{\sqrt{\pi}}\sqrt{\frac{tD}{d^2}}\,. \qquad (1)$$

The observed linearity of the curves in Fig. 1, extending to $(\Delta m)_t/(\Delta m)_\infty \approx 0.6$, and the curvature concave to the abscissa axis following the linear rise suggest a Fickian behavior of the sorption-desorption process with approximately h-independent diffusion coefficient (Fujita, 1968). From the initial slope of the curves of Fig. 1, the diffusion coefficient was calculated according to Eq. 1 and was found to be in the range of 2.4×10^{-11} to 3.7×10^{-11} m^2/s, the value for beans being about 20% lower than the one for wheat and values evaluated for sorption being somewhat higher than values for desorption. The experimental error in D is estimated to be about 15%.

Furthermore, using the approximate equation

$$(\Delta m)_t/(\Delta m)_\infty = 1 - exp\left[-7.3\left(\frac{Dt}{d^2}\right)^{0.75}\right], \qquad (2)$$

which is more suitable for moderate and larger times and which for $(\Delta m)_t/(\Delta m)_\infty = 0.5$ becomes

$$D = \frac{0.04919}{(t/d^2)_{0.5}}, \qquad (3)$$

where $(t/d^2)_{0.5}$ corresponds to the time where $(\Delta m)_t/(\Delta m)_\infty = 0.5$, we get D values in the range $1.4–2.8 \times 10^{-11}$ m^2/s. These values, determined in compressed seed flowers, are one order of magnitude lower than the ones determined in intact fresh wheat seeds by kinetic analysis of the movement of tritiated water (THO) through the grain and by NMR procedures, which were found to be of the order of 5×10^{-10} m^2/s (Ratkovič, 1987). The temperature dependence of D was not investigated in this study.

Thermally stimulated depolarization currents

Several TSDC measurements have been performed with all seed samples reported above, and various techniques offered by the TSDC method have been used to investigate the behavior of samples with different water contents. A typical TSDC plot, recorded for wheat samples with water contents h equal to 0.08, 0.13 and 0.21, respectively, is shown in Fig. 2. Two main dispersions are seen to contribute to the recorded thermogram: a broad, low-temperature (LT) band and a high-temperature (HT) one. With increasing water content both peaks increase in magnitude and shift to lower temperatures, i.e., the corresponding mechanisms become faster and more important. This is illustrated in Figs. 3 and 4, which show, respectively, the normalized maximum current I_n and the peak temperature T_m, for the low-temperature peak as a function of the water content h measured on bean seeds. More specifically, I_n is defined as the current maximum divided by the heating rate and polarizing field and is a measure of the number of relaxing units contributing to the peak (Pissis et al., 1991). The dependence of the high-temperature peak position on h is also shown in Fig. 4.

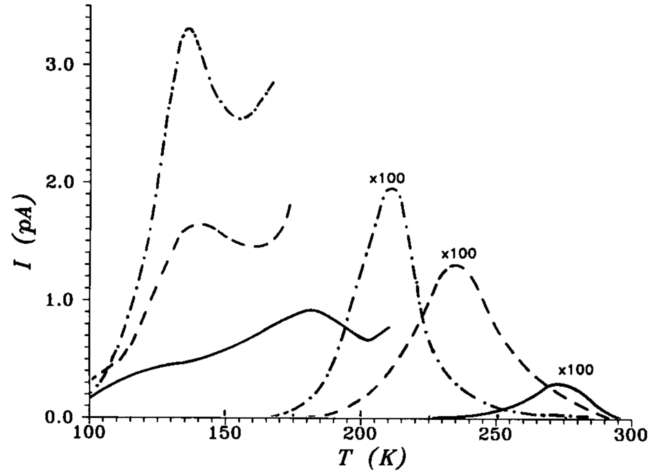

FIGURE 2 Thermally stimulated depolarization current (TSDC) spectra recorded on wheat flour samples with three different water contents h (g water/g dry material): 0.21 g/g (–·–·–), 0.13 g/g (– – –), 0.08 g/g (——).

The broad, low-temperature (LT) peak apparent even at very low water contents (h = 0.05%) is attributed to the reorientation of short side chains of the seed constituents (mainly carbohydrates and proteins) plasticized by water and is recorded with all similar substances (Anagnostopoulou-Konsta and Pissis, 1987; Pissis and Anagnostopoulou-Konsta, 1985). The plasticizing effect of water is demon-

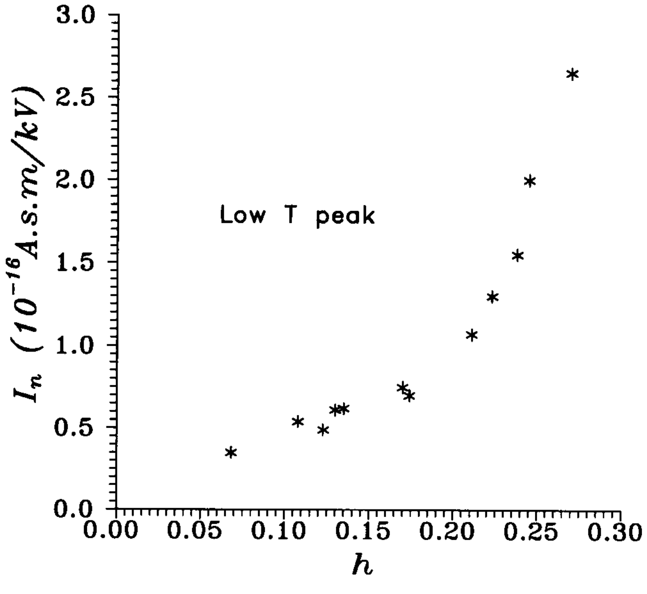

FIGURE 3 Dependence of the normalized current maximum I_n of the low temperature band on the water content h (in g water/g dry material) for different bean samples.

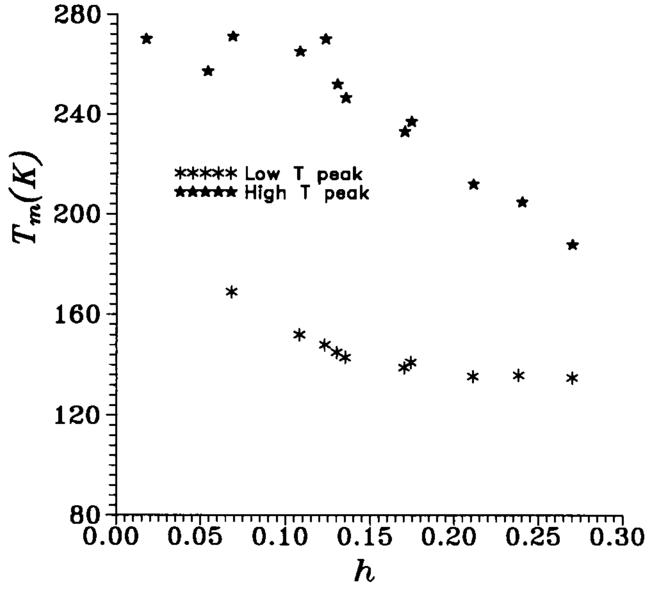

FIGURE 4 Dependence of the peak temperature $T_{\rm m}$ of the low (*) and the high (★) temperature band on the water content h (in g/g) for different bean samples.

strated by the displacement of this peak toward the lower temperatures with increasing h.

At higher water contents a new contribution, located at 135 K, appears. In fact, the large increase in the current maximum (Fig. 3) and the leveling of the peak temperature $T_{\rm m}$ for $h > 17\%$ (Fig. 4) cannot be interpreted in terms of plasticization only. Comparison with results of TSDC measurements in a very large number of biological and organic materials, in the solid and solution states (Pissis et al., 1987a,b; Anagnostopoulou-Konsta et al., 1991), indicates that this additional mechanism is due to the relaxation of loosely bound water molecules. It appears at about $h = 11\%$ for bean flour and 17% for wheat flour, as shown by a systematic investigation of the shape of the TSDC spectrum as a function of hydration. Thus, water up to $h = 0.17$ and 0.11 for bean and wheat, respectively, is tightly (irrotationally) bound to primary hydration sites (Pissis et al., 1987a), and there is no fraction of dielectrically free water up to the highest h-values studied.

The finding that beans bind a larger amount of water than wheat is easily understood, considering the fact that beans are much richer in proteins than wheat (which consists mainly of carbohydrates) and these proteins present more hydration (polar) sites than carbohydrates (Anagnostopoulou-Konsta and Pissis, 1987; Pissis and Anagnostopoulou-Konsta, 1985). NMR measurements at temperatures higher than 0°C, to be reported elsewhere, confirm this result.

The high-temperature band (Figs. 2 and 4) is attributed to the motion of the main carbohydrate and protein chains, plasticized by water, as well as to water-assisted charge relaxation or transfer (Pissis and Anagnostopoulou-Konsta, 1991; Bruni et al., 1989) related to DC conductivity. The temperature of the peak maximum is believed to be a measure of a glass transition temperature of the seed constituents, as supported by other findings (Pissis et al., 1992). The behavior of the HT peak clearly shows that the glass transition temperature T_g shifts to higher temperatures as the seed is dehydrated, analogously to the glass transition temperature of hydrated polymers (Kyritsis et al., 1994), and tends to room temperatures for very low-water contents. In fact, water acts as a plasticizer, increasing the mobility of the seed constituents, thus facilitating the transition from the glassy to the "rubbery" state as more water is added to the sample. The above findings are in qualitative agreement with all data reported in the literature. For example, according to differential scanning calorimetry (DSC) measurements in corn embryos (Williams and Leopold, 1989), at low water content glass transition occurs at +40°C and systematically falls to below −60°C as the water content rises to 20%. Similar results have been reported from the investigation of the behavior of mechanical properties of a variety of materials of natural and synthetic origin as a function of water content (Peleg, 1993; Singh et al., 1991) and from thermal (Vertucci, 1990) and EPR (Bruni and Leopold, 1991) measurements.

AC dielectric spectroscopy

Fig. 5, *a*, *b*, *c*, shows, respectively, the dependence of ϵ' (real part of the dielectric permittivity), ϵ'' (imaginary part), and AC conductivity G on frequency and temperature for a bean flour sample with 11% water content, and Fig. 6 shows the respective spectra for wheat flour with approximately the same hydration. Both samples correspond to room RH conditions. The essential remarks concerning the relaxation spectroscopy results are as follows.

The main relaxation dispersion, which is displaced toward the lower frequencies with decreasing temperature, is attributed principally to the motion of short side chains plasticized by water. Its origin is the same with the broad LT dispersion of the TSDC spectrum, visible for low h, as verified by extrapolation of the $\ln f_{\rm m}$ versus $1/T$ straight line (Arrhenius plot, shown in Fig. 7 for bean seeds) at 143 K and assuming an equivalent frequency of 2.5×10^{-2} Hz. Its activation energy is found to be equal to

$$w = 0.54 \pm 0.05\ eV$$

or, equivalently,

$$w = 52 \pm 5\ \text{kJ/mol} = 12 \pm 1\ \text{kcal/mol}.$$

Practically the same value for the activation energy of this mechanism results from the Arrhenius plot of the tan D peak ($\tan D = \epsilon''/\epsilon'$), as shown in the same figure. As in TSDC, the behavior of this peak is practically independent of the seed nature.

The part of the spectrum corresponding to low frequencies (lower than 100 kHz for $h = 12$–13%) is believed to have the same origin as the HT peak of TSDC, i.e., long main chain relaxation, space charge effects, and charge

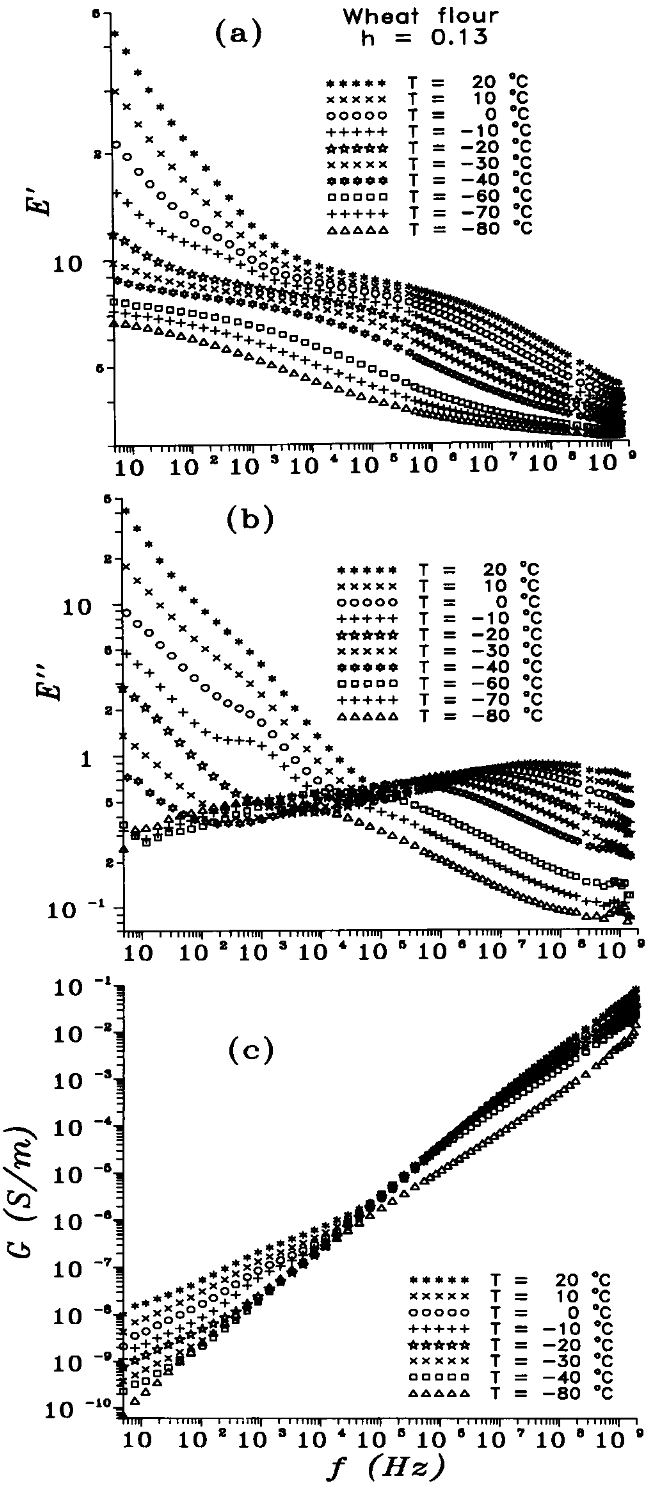

FIGURE 5 The dependence of ϵ′ (*a*), ϵ″ (*b*), and conductivity *G* (*c*) of a wheat flour sample with *h* = 0.13 g/g on the electric field frequency *f*, recorded at different temperatures.

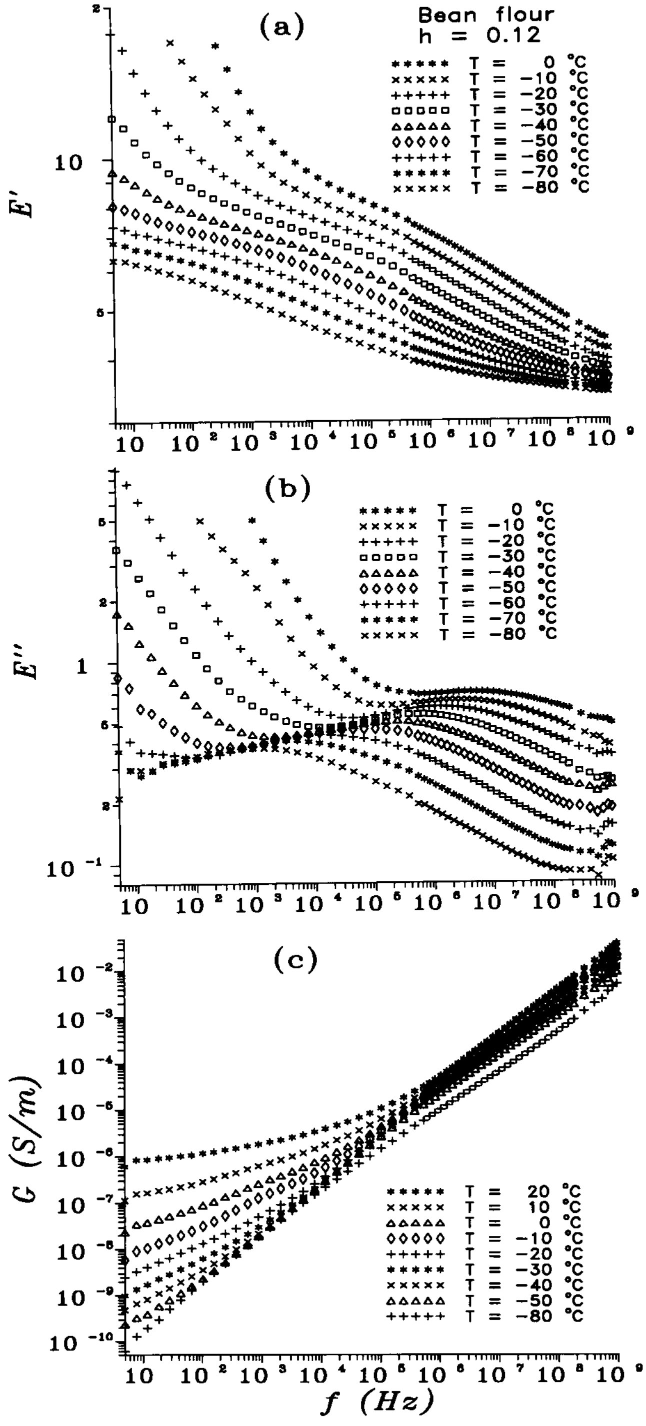

FIGURE 6 The dependence of ϵ′ (*a*), ϵ″ (*b*), and conductivity *G* (*c*) of a bean flour sample with *h* = 0.12 g/g on the electric field frequency *f*, recorded at different temperatures.

carriers motion giving rise to conductivity (Carreri and Giasanti, 1984). Moreover, at low frequencies and relatively high water contents we observe the effects of blocking electrodes. Both bulk and surface effects contribute to the plots in Figs. 5 and 6. The high values of ϵ′ at low frequencies indicate the existence of the so-called space-charge polarization (Macdonald, 1973). On the other hand, the apparent dielectric loss becomes very high at low frequencies and high water contents. This is not the bulk dipolar dielectric loss, but rather is due to the free charge motion

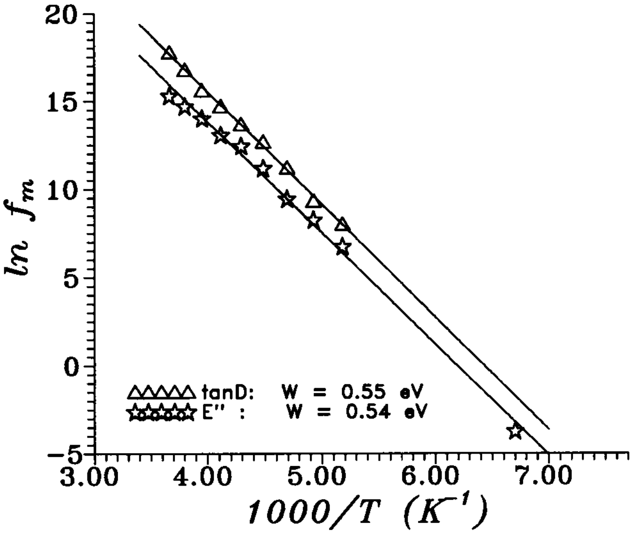

FIGURE 7 Arrhenius plot, i.e., the $\ln f_m$ versus $1/T$ plot, where f_m is the frequency (in hertz) corresponding to the maximum of ϵ'' and tan D, respectively, for a bean flour sample with $h = 0.12$ g/g, evaluated from the spectra of Fig. 6 *b*. The last point on the right corresponds to the LT peak of the TSDC plot, recorded with an identical sample.

within the material (conductivity relaxation) (Starkweather and Avakian, 1992).

No interpretation has been found for the small dispersion appearing at 1000 Hz in wheat samples (Fig. 5), which disappears for temperatures lower than −10°C, and which for higher water contents is masked by the contribution of the DC conductivity due to water molecules themselves. In fact, as the water content increases (Figs. 8–10), a large overall increase of the low-frequency conductivity is observed. The chemical composition of the sample has almost no influence on the recorded spectra, which are now dominated mainly by the water contribution.

It is interesting to note, however, that the decrease of the low-frequency conductivity with temperature, for temperatures lower than 0°C, is gradual and gives no indication of a sudden crystallization of loosely bound water, at least up to $h = 30\%$ (Fig. 8). Only at higher h values does the conductivity change abruptly at a certain critical temperature from typical conductor-like to typical insulator-like behavior (Fig. 9). Above the critical temperature the conductivity is of pure DC type, effected via water molecule pathways in the sample, whereas below that temperature the water has crystallized, there is no net charge transfer in the sample, and the conductivity is of the typical AC type. Taking as the temperature of onset of freezing the one at which discontinuity occurs, we find that this critical temperature increases with water content.

The difference between spectra taken with decreasing and increasing T is shown in Fig. 10 for a bean seed sample containing 36% water. Spectra recorded with decreasing T show that water freezes between −30 and −40°C, whereas if the process is reversed, liquid water starts to form above −20°C. The irreversibility of the freezing-defreezing process when water is confined in a limited space is of course well known, but it is interesting to note that dielectric spectroscopy provides a very sensitive technique for detecting it.

All of the above findings are in good agreement with results reported in the literature. In fact, Vertucci (1990),

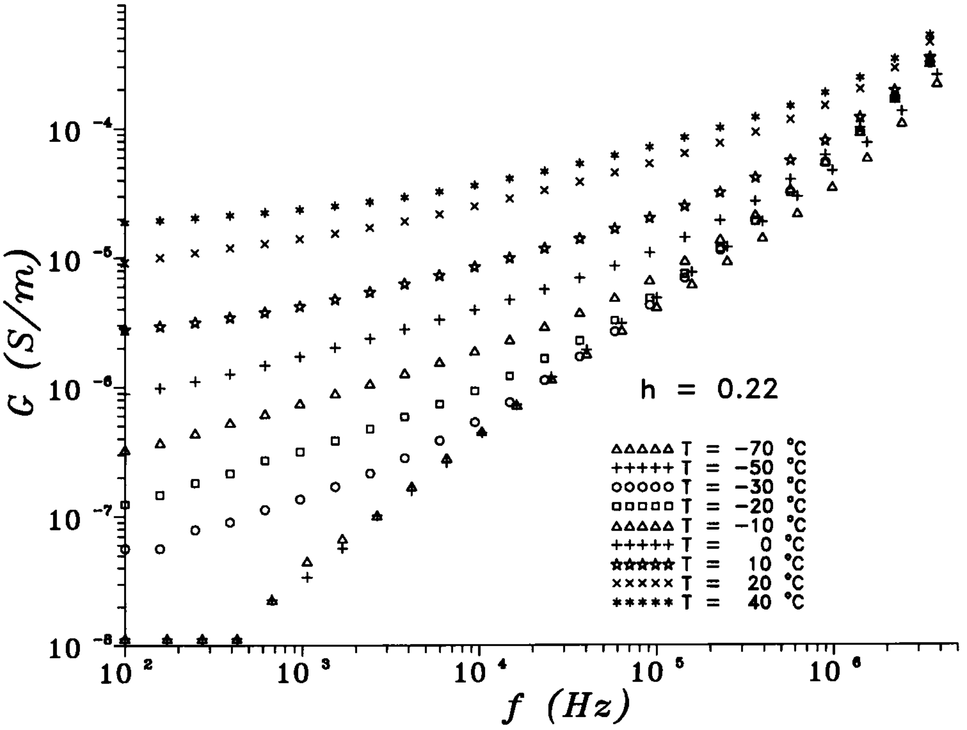

FIGURE 8 The dependence of the conductivity spectra on temperature for a wheat flour sample with $h = 0.22$ g/g.

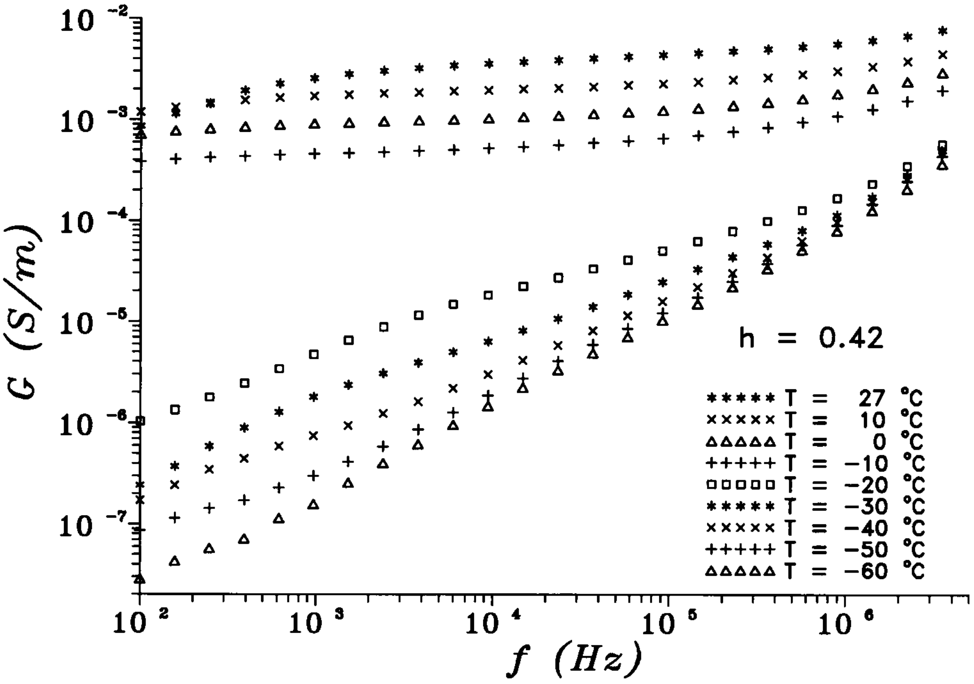

FIGURE 9 Evidence of water crystallization at $-10 < T < -20$°C, for a wheat flour sample with an initial 0.42 g/g water content.

who has performed calorimetric studies of water in seed tissues, has also found that freezing of water was not observed till h reached 0.33–0.35. At lower water contents water seemed to undergo a glass-like transition instead of or before melting. The temperature of freezing and melting varied with h and showed hysteresis; only for $h > 0.54$–0.58 did the melting properties of water resemble those of pure water or water in dilute solutions.

The dependence of the conductivity spectra on water content at constant temperature is shown in Fig. 11. It is seen that broad-band dielectric spectroscopy may be used to determine the moisture content in seed samples by exploiting the lower part of the frequency range of our experiments. This may prove an interesting alternative to measurements at higher frequencies (Kraszewski and Nelson, 1989, 1993; Nelson, 1994a).

Finally, Fig. 12 displays the evolution of the conductivity spectrum as a function of time for a hydrated seed sample kept at 40°C for 300 min, evidence of the dehydration of the sample from an initial 24% to a final 5% water content.

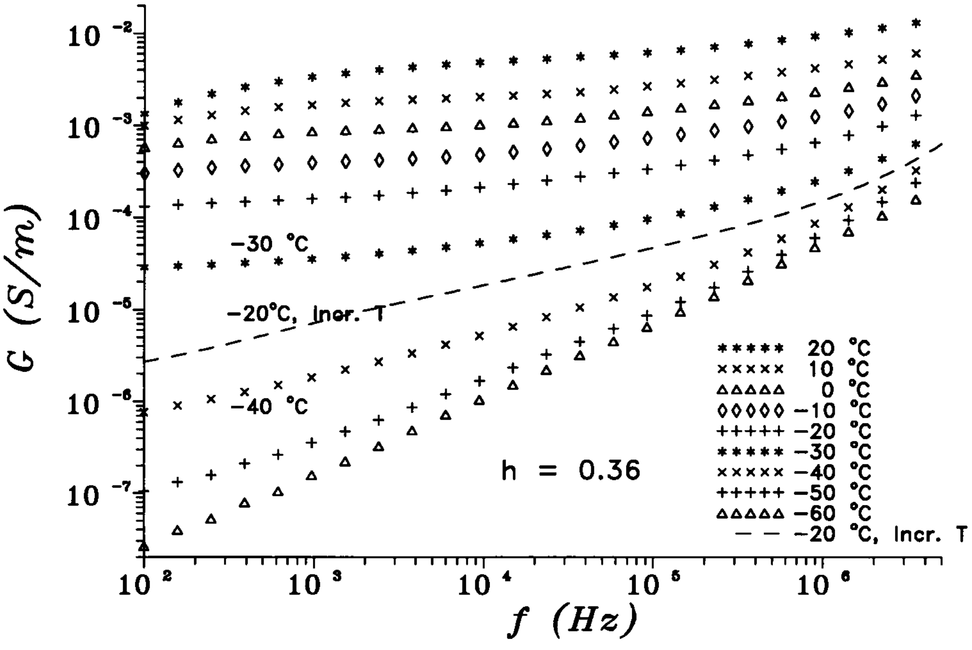

FIGURE 10 The dependence of the conductivity spectra on temperature, recorded with decreasing T, for a bean flour sample with $h = 0.36$ g/g. The dashed-line curve was recorded with increasing T. The irreversibility of the freezing-melting process is clearly demonstrated.

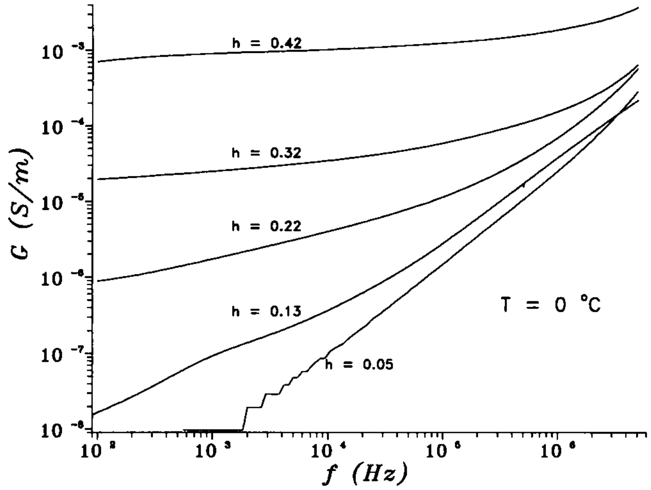

FIGURE 11 Dependence of the conductivity spectra of wheat flour samples on their water content, at $T = 0°C$.

We note the similarity between Figs. 8 and 10 or 9 and 11. An increase in temperature T at constant water content h causes the same effect as an increase in h at constant T. These findings are a manifestation of the *T-f-h* superposition principle, already proposed for hydrated polymers (Starkweather, 1980), which states that the plasticizing effect of increasing water content at constant T is equivalent to the effect of increasing T at constant h, both leading to enhancement of molecular and charge mobility.

As a final remark on all of the spectra recorded with highly hydrated samples, we note a drop of the apparent conductivity at low frequencies below its DC value (Figs. 9–12, for $T > 0°C$), a clear indication of the electrode polarization effect, i.e., the accumulation of charges on the sample-electrode interface, due to the "free" charge motion within the material (Bone and Zaba, 1992; Schwan, 1992).

CONCLUSIONS

In conclusion, our results have made it possible to do the following:

to estimate the diffusion constant of the water molecules in our samples, which has been found to be of the order of 10^{-11} m^2/s;

to determine a critical water content corresponding to the completion of the primary hydration layer (the tightly bound water fraction), and show that in protein-rich seeds this fraction is higher than in carbohydrate-rich seeds;

to evaluate the activation energy of the main relaxation process, which has been found to be equal to 0.54 ± 0.05 eV (52 ± 5 kJ/mol);

to study the dependence of various parameters (conductivity, molecular mobility, plasticizing effect of water) on the water content of the sample;

to follow the crystallization of water in seeds as a function of temperature and confirm that it is not a reversible process;

to study the dehydration process as a function of temperature and time;

to propose, finally, an alternative technique for the determination of the water content in seeds with the use of AC dielectric spectroscopy for frequencies lower than about 100 kHz.

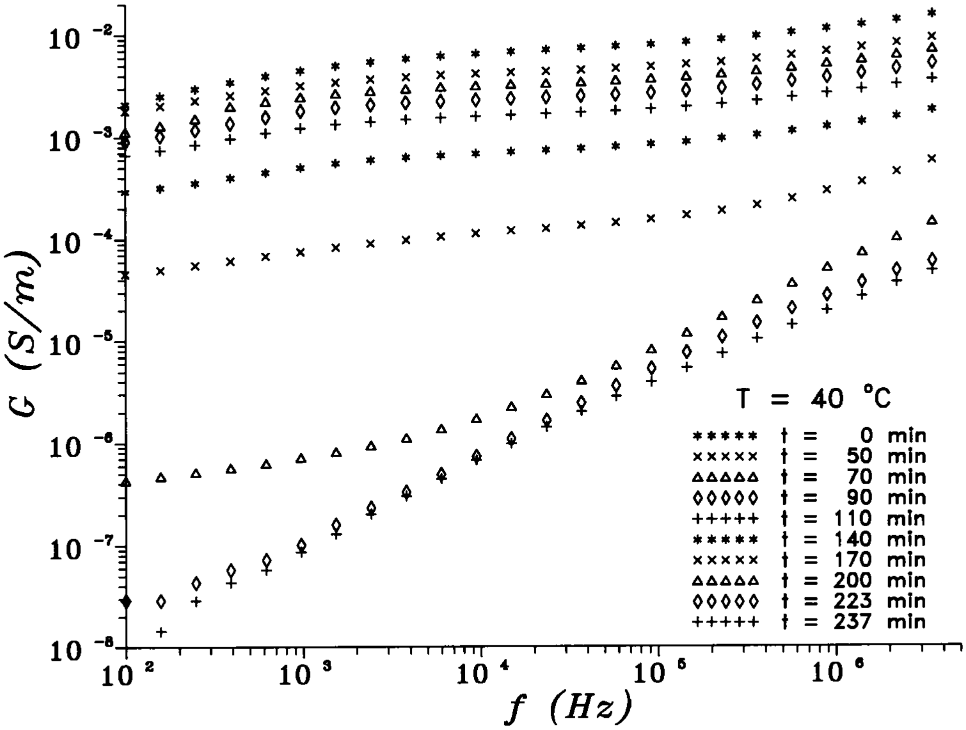

FIGURE 12 Evolution of the conductivity spectrum of a bean flour sample during its dehydration at 40°C, from an initial water content of 0.36 g/g to a final one of 0.09 g/g.

Thanks are due to Antoine Letoublon, Erasmus student, and Rolf Pelster and Volker Grunow from the University of Cologne, for very helpful assistance in data acquisition and processing.

A grant of the Empirikos Foundation is gratefully acknowledged.

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