

DIELECTRIC BEHAVIOUR OF ICE MICROCRYSTALS: A STUDY VERSUS TEMPERATURE*

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ABSTRACT. Dispersions of ice microcrystals were obtained from the breakdown of supercooling of water-in-oil type emulsions whose disperse phase was either resin-exchanged water or aqueous solutions of NH_4Cl . Their complex permittivity $\epsilon^* = \epsilon' - j\epsilon''$ was studied versus temperature T , up to the melting point of ice microcrystals, by means of an automatically balancing admittance bridge (General Radio 1 680 A) working at 400 Hz and 1 kHz. The plots $\epsilon'(T)$, $\epsilon''(T)$, and $\epsilon''(\epsilon')$ reveal that these systems exhibit two distinct dielectric relaxations located on either side of a temperature T_m which was found to be equal to about -20°C in the case of water and lower than -20°C in the case of aqueous solutions of NH_4Cl . The relaxation located in the lower temperature range arises from the Debye dipolar absorption of ice while the other one could be related to structural changes occurring within the lattice of ice as T approaches its melting point. These results are consistent with those obtained by investigating versus frequency the dielectric behaviour of ice microcrystals at discrete sub-zero temperatures close to their melting point.

RÉSUMÉ. Propriétés diélectriques des dispersions de microcristaux de glace: étude en fonction de la température. Des dispersions de microcristaux de glace ont été obtenues par rupture de surfusion des gouttelettes d'émulsions dont la phase dispersée est de l'eau permutée ou une solution aqueuse de NH_4Cl . Leur permittivité complexe $\epsilon^* = \epsilon' - j\epsilon''$ a été étudiée en fonction de la température T , jusqu'au voisinage de la température de fusion des microcristaux de glace, au moyen d'un pont automatique General Radio 1 680 A, aux fréquences de 400 Hz et 1 kHz. Les courbes $\epsilon'(T)$, $\epsilon''(T)$ et $\epsilon''(\epsilon')$ montrent que ces systèmes présentent deux domaines de relaxation distincts, situés de part et d'autre d'une température T_m , égale à -20°C environ dans le cas de l'eau et plus basse que -20°C dans le cas des solutions aqueuses de NH_4Cl . La relaxation située aux températures les plus basses est due à l'absorption dipolaire Debye de la glace, alors que l'autre est certainement à relier à des modifications de structure intervenant dans le réseau de la glace lorsque T approche de la température de fusion. Ces résultats sont en accord avec ceux obtenus en étudiant en fonction de la fréquence les propriétés diélectriques de dispersions de microcristaux de glace, à des températures fixes voisines du point de fusion.

ZUSAMMENFASSUNG. Dielektrisches Verhalten von Eis-Mikrokristallen: eine Untersuchung in Abhängigkeit von der Temperatur. Dispersionen von Eis-Mikrokristallen wurden beim Zusammenbruch der Unterkühlung von Emulsionen des Typs "Wasser in Öl" gewonnen; ihre disperse Phase war entweder ionenausgetauschtes Wasser oder wässrige Lösungen von NH_4Cl . Ihre komplexe Dielektrizitätskonstante $\epsilon^* = \epsilon' - j\epsilon''$ wurde in Abhängigkeit ihrer Temperatur T untersucht, besonders in der Nachbarschaft des Schmelzpunktes der Eis-Mikrokristalle. Dazu wurde eine selbständig abgleichende Admittanzbrücke (General Radio 1 680 A) verwendet, die bei 400 Hz und 1 kHz arbeitet. Die Diagramme $\epsilon'(T)$, $\epsilon''(T)$ und $\epsilon''(\epsilon')$ zeigen, dass diese Systeme zwei ausgeprägte dielektrische Relaxationen zu beiden Seiten einer Temperatur T_m aufweisen. Diese wurde bei Wasser zu ungefähr -20°C und tiefer als -20°C bei wässrigen NH_4Cl -Lösungen festgestellt. Die Relaxation im niedrigeren Temperaturbereich stammt von der Debye'schen dipolaren Absorption des Eises, während die andere strukturellen Änderungen innerhalb des Eisgitters zugeordnet werden konnte, die eintreten wenn T sich dem Schmelzpunkt nähert. Diese Ergebnisse stimmen mit denjenigen überein, die bei der Untersuchung des dielektrischen Verhaltens der Eis-Mikrokristalle in Abhängigkeit von der Frequenz bei bestimmten Temperaturen unterhalb Null dicht beim Schmelzpunkt erhalten wurden.

INTRODUCTION

Many studies have been devoted to the dielectric and conduction properties of ice in order to obtain information about its internal structure. Most of them concern either monocrystalline or polycrystalline ice samples a few cm^3 in volume whose behaviour was investigated under various conditions of temperature, pressure, and ion incorporation.

Other studies deal with dispersions of ice particles a few μm^3 in volume obtained from the breakdown of supercooling of water-in-oil type emulsions. Results in this field have been reported by Evrard (unpublished [b]) and Evrard and others (1974[a], [b]), who showed that dispersions of ice microcrystals can exhibit two distinct dielectric relaxations. A detailed

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study of this phenomenon has been published recently by Lagourette (1976, unpublished), who investigated the complex permittivity of dispersions of ice particles versus the frequency of the applied electrical field, at discrete sub-zero temperatures. According to this author, the dielectric relaxation located in the higher frequency range can be related to the Debye dielectric absorption of ice. Between 0°C and -20°C an additional dielectric relaxation, located in the lower frequency range, is noticeable. When the temperature decreases, the intensity of this extra relaxation decreases and eventually vanishes at about -20°C . Moreover, as is shown in Figure 1, it is not possible to define an energy of activation for this relaxation, as the plot of $\log \nu_{c2}$, (ν_{c2} being the critical frequency), versus T^{-1} is not a straight line. It is worth mentioning that, correspondingly, it is not possible between 0°C and -20°C to define an energy of activation for the relaxation located in the higher frequency range.

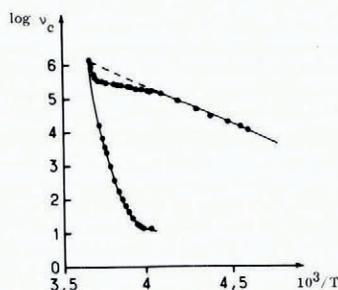


Fig. 1. Plots of $\log \nu_c$ versus T^{-1} . Mass fraction of disperse water: $p = 0.28$.

A tentative explanation of these phenomena has been given by Lagourette and others (1976) from computer calculations based on a theoretical model that has proved suitable for emulsion systems (Hanaï, 1968; M. Clause and Royer, 1976). Lagourette and others propose that, as the temperature approaches the melting point of ice microcrystals, the ice crystal lattice undergoes local structural changes leading to the formation of non-crystalline conductive clusters within it.

In an attempt to give a further contribution to the understanding of the phenomena briefly reported above, a study has been undertaken which concerns the variations of the complex permittivity of dispersions of ice microcrystals versus their temperature.

EXPERIMENTAL PROCEDURE

(1) Sample preparation

Water-in-oil type emulsions were made by dispersing in a mixture of 25% (wt/wt) lanolin (Prolabo R.P.) and 75% (wt/wt) vaseline oil (Prolabo R.P.) resin-exchanged water or aqueous solutions of analysis-grade ammonium chloride. The emulsification process was carried out at room temperature by means of a propeller-type homogenizer working at 45 000 r.p.m. Each emulsion was characterized by a mass fraction p of disperse aqueous phase and, in the case of saline solutions, by a molar fraction x of solubilized ammonium chloride. For values of p less than 0.6, the emulsions obtained through this method consist of dispersions of droplets a few micrometres in diameter, the distribution of droplet sizes being very narrow, as proved by microscope observation (Lagourette, 1976, unpublished).

Owing to the small droplet sizes, large supercoolings of the disperse water can be obtained. For instance, Evrard (unpublished [a]) found that the freezing of water occurs in such systems around -39°C . Later on, this author claimed a freezing temperature of -41°C (Evrard, 1973, unpublished [b]). A statistical analysis of the freezing temperature of water

dispersed within emulsions was made by Boned ([1968], unpublished [a]), from DTA measurements on 600 different samples. He obtained a mean value of -38.5°C and observed that freezing temperatures lower than -40°C occur very seldom. The value of -38.5°C was also reported by Lafargue and Babin (1964) and Babin (unpublished), who investigated the breakdown of supercooling of water dispersed within emulsions through dielectric measurements. It has been recently confirmed by D. Clause (1976) from DEA measurements made by means of a Perkin-Elmer DSC 2 calorimeter.

A freshly made emulsion was poured into the dielectric measuring cell which was placed immediately into a temperature-controlled chamber. The cell was cooled down to about -150°C and then heated up to near the melting point of the disperse phase. The rate of cooling was -1.5 deg/min, the rate of heating being 0.5 deg/min. Some samples were frozen very rapidly by immersing the cell in liquid nitrogen. Their dielectric behaviour was the same as that of steadily cooled samples.

The temperature T of the samples was recorded to within ± 0.5 deg by means of a calibrated thermocouple fitted into a cavity drilled within the volume of the outer electrode of the cell.

(2) Dielectric measurements

The dielectric behaviour of the samples was investigated during the initial cooling, then during the following heating and, sometimes, during a subsequent cooling. The dielectric cell used consists mainly of a cylindrico-conical capacitor made of stainless steel and especially designed for the study of liquids (Ferisol CS 601). The active capacity of the cell C_a is 10 pF at 20°C , the gap between the electrodes being 3 mm. The variations of C_a with temperature ($\Delta C_a/\Delta T = 0.5 \times 10^{-3}$ pF/deg), were taken into account for the determination of the real permittivity and loss factor of the samples.

The complex relative permittivity $\epsilon^* = \epsilon' - j\epsilon''$ of the samples was determined at either 400 Hz or 1 kHz by means of a General Radio 1680 A automatically-balancing admittance bridge connected to a two-channel Esterline-Angus E 1102 E data recorder, the maximum value of the voltage applied between the cell electrodes being equal to 1 V. The uncertainty upon both ϵ' and ϵ'' was estimated to be less than 1% .

RESULTS

(a) Dielectric behaviour of dispersions of ice microcrystals obtained from emulsions of water

A freshly-made water-in-oil sample having been poured into the measuring cell, its complex permittivity $\epsilon^* = \epsilon' - j\epsilon''$ was recorded during continuous cooling down to about -150°C . Owing to the discrepancy existing between the dielectric properties of water and ice, the breakdown of supercooling of the disperse droplets can be easily detected from the sudden decrease of ϵ' and increase of ϵ'' . As the temperature is lowered, the frozen emulsion exhibits a dielectric relaxation arising from the Debye dipolar absorption of the disperse ice particles.

During the following heating from -150°C up to near 0°C , the study of the complex permittivity reveals the existence of two dielectric relaxations located either side of a temperature T_m , as shown in Figure 2 which represents the plots of ϵ'' and ϵ' versus T obtained in the case of a dispersion characterized by a mass fraction of water (or ice) equal to 0.40 .

The relaxation located in the lower temperature range will be referred to as R_1 and the relaxation located in the higher temperature range as R_2 , T_{c_1} and T_{c_2} being the temperatures corresponding to the respective maximal values of ϵ'' .

From Figure 3, which gives the variations of $\epsilon''(T)$ versus $\epsilon'(T)$, some characteristic features of the phenomenon can be seen. Experiments show that R_1 is similar to the relaxation

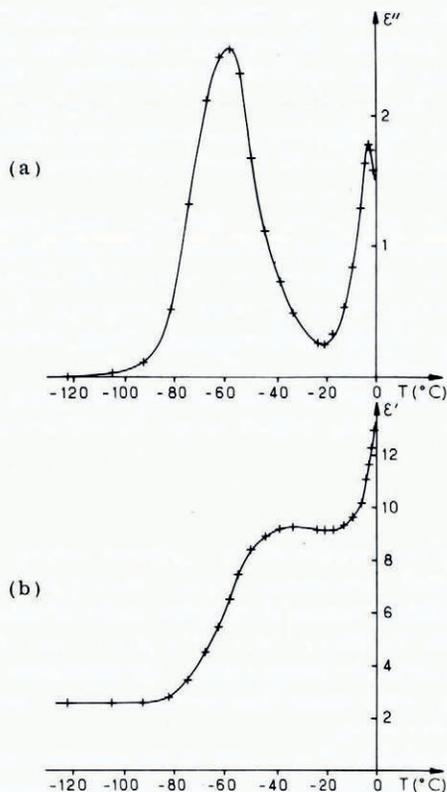


Fig. 2. Variations of (a) ϵ'' and (b) ϵ' versus T . Mass fraction of disperse water: $p = 0.40$. Frequency: $\nu = 400$ Hz.

observed during the initial cooling, after the breakdown of supercooling has occurred. Up to about -50°C , the part of the diagram representative of R_1 is a circular arc, while at higher temperatures the points $\epsilon''(\epsilon')$ lie below this circular arc. The connection with that part of the diagram representative of R_2 is formed, in most of the cases, by a loop.

The features of both R_1 and R_2 depend upon the value of p , the mass fraction of disperse ice. For values of p up to 0.43, the intensity of R_1 is greater than that of R_2 while it is the reverse for values of p greater than 0.43. As regards the critical temperatures T_{c1} and T_{c2} , both of them are higher the greater the value of p (Table I), T_m remaining equal to -20°C to within ± 0.5 deg.

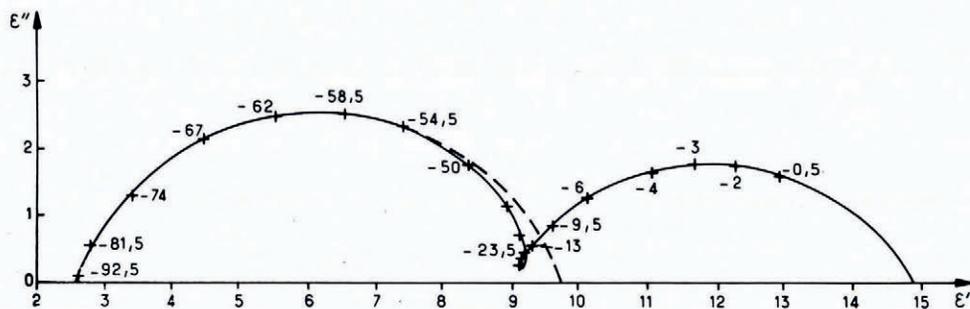


Fig. 3. Variation of ϵ'' versus ϵ' . Mass fraction of disperse water: $p = 0.40$. Frequency: $\nu = 400$ Hz.

TABLE I. VARIATIONS OF T_{c_1} AND T_{c_2} WITH p ($\nu = 1$ kHz)

p	0.10	0.33	0.40	0.60
T_{c_1} K	210	213.5	222.5	228
T_{c_2} K	262	268.5	271.5	272.5

For $\nu = 400$ Hz, the values found for T_{c_1} and T_{c_2} are smaller. For instance, with $p = 0.40$, $T_{c_1} = 213$ K and $T_{c_2} = 270$ K. This is consistent with the observations made by Lagourette (unpublished) during his study of ice dispersions versus frequency at discrete sub-zero temperatures.

(b) *Dielectric behaviour of dispersions of ice microcrystals obtained from emulsions of aqueous solutions of NH_4Cl*

A similar study has been carried out in the case of ice dispersions obtained from the breakdown of supercooling of emulsions of aqueous solutions of NH_4Cl , in order to complement the investigations made in this field by Boned (unpublished [b]) and Boned and others (1976). Moreover, the metastable phase behaviour of aqueous solutions of NH_4Cl has been thoroughly studied (D. Clause, 1976), and is well known.

As is shown on Figure 4, the general behaviour of these systems is qualitatively similar to that exhibited by dispersions of ice obtained from emulsions of water, in particular as concerns the lower-temperature relaxation R_1 , which is shifted towards lower temperatures. The salt concentration x has a marked influence upon the features of R_2 whose intensity increases with x while T_{c_2} and T_m decrease (Table II).

Some experiments have shown that a similar behaviour can be observed in the case of ice dispersions obtained from emulsions of aqueous solutions of NH_4NO_3 .

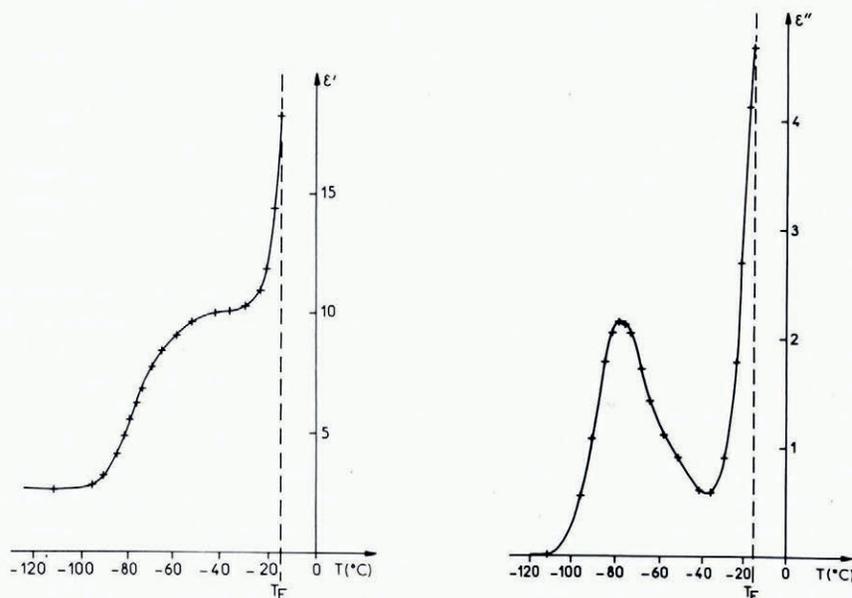


Fig. 4. Variations of (a) ϵ' and (b) ϵ'' versus T . Concentration of NH_4Cl : $x = 7.4 \times 10^{-2} = x_E$ (eutectic concentration). Mass fraction of disperse phase: $p = 0.40$. Frequency: $\nu = 1$ 000 Hz.

TABLE II. VARIATIONS OF T_{c_2} AND T_m WITH x ($p = 0.40$, $\nu = 1$ kHz)

x	0	1.8×10^{-5}	1.8×10^{-4}	7.4×10^{-2} *
T_{c_2} °C	-1.5	-3.5	-13	-15.5
T_m °C	-20	-23	-30	-38

* Eutectic concentration.

DISCUSSION

The results that have just been reported concerning the dielectric behaviour of dispersions of ice microcrystals versus temperature are consistent with those obtained by Lagourette (1976, unpublished) who investigated versus frequency, at discrete sub-zero temperatures, the dielectric properties of that kind of system.

Figure 5 is a Cole-Cole plot of a dispersion of ice microcrystals ($p = 0.40$) studied versus frequency at -8°C , one hour or so after the breakdown of supercooling had occurred. A comparison of Figures 3 and 5 shows that R_1 is similar to the higher frequency relaxation observed by Lagourette and R_2 to the lower frequency one.

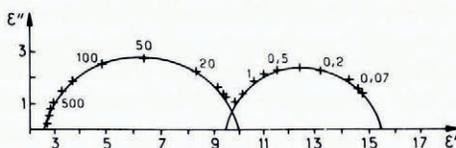


Fig. 5. Cole-Cole plot of a dispersion of ice microcrystals studied one hour after the breakdown of supercooling. $T = -8^\circ\text{C}$, $p = 0.40$. The frequency ν is given in kHz.

In the $\epsilon''(T)$ versus $\epsilon'(T)$ plot, the part of the diagram representing R_1 is distorted at higher temperatures and, in most of the cases, is connected to that representing R_2 by a loop that can be ascribed to a decrease of the static permittivity ϵ_s of ice upon increasing the temperature. This kind of phenomenon has been studied both experimentally and theoretically by different authors (Le Montagner, 1960; Sixou and others, 1967; Demau and others, 1971). For a substance whose static permittivity is a decreasing function of the temperature T , these authors proved that, when T increases, the real part ϵ' of the complex permittivity recorded at a given frequency increases, reaches a maximum value and then decreases, which leads to a distortion of the ϵ'' versus ϵ' diagram and to the formation of a loop if a further relaxation exists in the higher temperature range. In the present case, the existence of a loop can be put into evidence from the data of the study made by Lagourette, by plotting, at a given frequency, 1 kHz for instance, the values of ϵ'' obtained at several temperatures ranging from -36°C up to -1°C against the corresponding values of ϵ' .

As concerns the activation energy, its values cannot be determined with great accuracy since, for substances whose static permittivity is strongly temperature dependent (like ice), it is difficult to evaluate correctly the activation energy from the $\epsilon''(T)$ versus $\epsilon'(T)$ plot, as Le Montagner (1960) and Sixou and others (1967) have stressed. For instance, the value found for R_1 (Fig. 3) is equal to 0.5 eV at most. This high value indicates that the state of evolution in time of the dielectric properties of this system, which was studied during a continuous heating just after the breakdown of supercooling, is not as advanced as that of the system corresponding to Figure 1, which was first heated up to near 0°C and then studied during a subsequent step-by-step cooling. This is in agreement with the observation made by Evrard (unpublished [b]) that the evolution in time of the dielectric properties of ice microcrystal dispersions is the faster the higher the peak reheating temperature. A similar conclusion was arrived at by Lagourette (unpublished) who found values of the activation energy ranging from about 0.40 eV to about 0.16 eV, whatever the mass fraction of disperse ice.

Similarly, the discrepancy existing between the $[-8^{\circ}\text{C}, 400\text{ Hz}]$ data points of Figures 3 and 5 can be ascribed to the slightly different age-temperature history of the samples. However, comparison of the ϵ'' versus ϵ' plots of Figures 3 and 5 shows clearly that the double relaxation phenomena found by Lagourette during fixed-temperature/variable-frequency experiments can be put into evidence as well as from fixed-frequency/variable-temperature investigations.

A freeze-etching study (Broto, unpublished) has shown that dispersions of ice microcrystals consist of individual spherical particles imbedded in the continuous phase of solidified oil (Fig. 6). This result justifies the application to ice dispersions of the formula proposed by Hanai (1968) to represent the complex permittivity of spherical dispersion systems:

$$\left(\frac{\epsilon_1^* - \epsilon_2^*}{\epsilon_1^* - \epsilon^*}\right)^3 \frac{\epsilon^*}{\epsilon_2^*} = \frac{1}{(1 - \Phi)^3}, \quad (1)$$

ϵ^* , ϵ_1^* , and ϵ_2^* represent the complex permittivity of the dispersion, of the disperse phase and of the continuous phase, respectively, Φ being the volume fraction of the disperse phase. By comparing experimental data and computer calculations, M. Clause (1972, unpublished) and M. Clause and Royer (1976), have established that the dielectric features of emulsions, particularly of the water-in-oil type, can be correctly represented by using Hanai's law and its derivative formulas.

A first attempt made by M. Clause (unpublished) in 1971 to apply Equation (1) to the study of dispersions of ice microcrystals proved that the dielectric behaviour of these systems cannot be explained by assuming that the ice microcrystals exhibit merely a bulk conduction in addition to a Debye dipolar absorption. While the experimental values of either the higher-frequency or the lower-temperature limiting permittivity are in agreement with the computed theoretical ones, discrepancies appear when dealing with the lower-frequency (or higher-

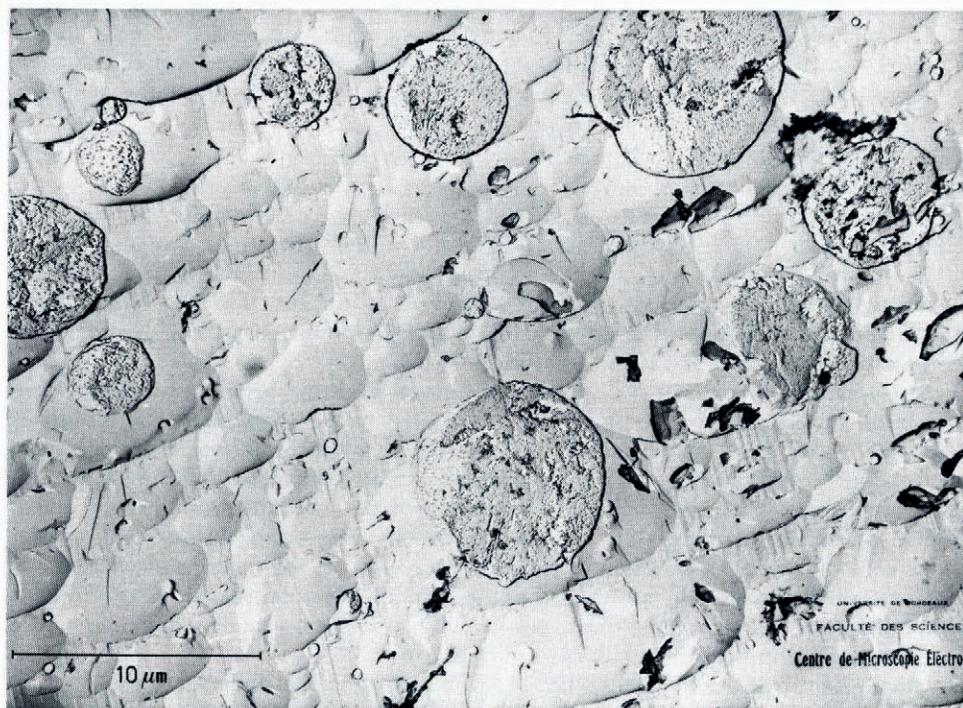


Fig. 6. Freeze-etching replica of a dispersion of ice microcrystals. $p = 0.20$; magnification: $3\ 260$.

temperature) limiting permittivity ϵ_1 . According to the theoretical model, ϵ_1 should be related to the volume fraction of disperse ice Φ by

$$\epsilon_1 = \epsilon_2 \frac{1}{(1-\Phi)^3}, \quad (2)$$

where ϵ_2 represents the static permittivity of the continuous phase. Since Φ and the static permittivity ϵ_2 of non-polar oil phases are almost constant in the temperature range concerned, ϵ_1 should be temperature independent as well. It was shown by Lagourette (1976) that ϵ_1 depends upon temperature within the range 0°C to -20°C and does not fit Equation (2). This result is consistent with the observations made during the present study. For instance, the experimental value of ϵ_1 corresponding to Figure 3 was found to be equal to 14.8 while the theoretical value is 10.1, the continuous phase permittivity ϵ_2 , almost temperature independent, being equal to 2.4, and the volume fraction of disperse ice Φ to 0.38.

A more sophisticated model has been designed by Lagourette and others (1976) to interpret the dielectric behaviour of dispersions of ice microcrystals, particularly as concerns the dependence of the lower-frequency relaxation upon temperature. The main hypothesis underlying the model is that, at temperatures higher than -20°C or so, clusters of disordered water molecules appear in the vicinity of the defects and dislocations of the ice lattice, the number of molecules involved increasing as the temperature approaches the melting point of ice. On this basis, by following a procedure proposed by M. Clause and Lachaise (1972) to study the dielectric properties of polydisperse systems, Lagourette and others (1976) have computed, through an application of Hanai's formula, a theoretical model that fits the experimental data satisfactorily and allowed them to derive the following conclusions:

- (i) the higher-frequency (or lower-temperature) dielectric relaxation exhibited by dispersions of ice microcrystals is connected to the Debye dipolar absorption of the ice lattice;
- (ii) the lower-frequency (or higher-temperature) dielectric relaxation could be ascribed to a so-called "pre-melting" phenomenon arising from the formation, in the vicinity of defects or dislocations in the ice lattice, of essentially conductive clusters of disordered molecules, the number and/or size of the clusters increasing as the temperature approaches the melting point of ice.

The so-called "pre-melting" of ice microcrystals is to be considered in connection with the various observations reported by several authors who have suggested the existence of near-liquid disordered clusters or films in ice, at temperatures close to the melting point (Jellinek, 1967; Bell and others, 1971; Fletcher, 1973; Kvlividze and others, 1974; Nason and Fletcher, 1975; Golecki and Jaccard, 1977; Perez and others, 1978). In a recent paper, Bartis (1977) has shown that the anomalous components acquired by the specific heat of a solid as its temperature approaches its melting point could be ascribed to the growth of "liquid" domains around point defects and along edge dislocations.

In the case of ice microcrystal dispersions obtained from the breakdown of supercooling of water-in-oil emulsions, it is most likely that, owing to the high degree of metastability reached ($\Delta T = 38.5$ deg), many defects are generated within the lattice of the ice particles during freezing. That would explain the striking effects of temperature upon the lower-frequency dielectric relaxation of ice microcrystal dispersions and justifies the claim by Lagourette and others (1976), that, just below the melting temperature, 30% of the ice molecules could belong to disordered clusters. Anyway, it has been proved from DEA measurements (Dumas and others, 1975), that the dependence upon temperature of the lower-frequency dielectric relaxation features cannot be ascribed to a partial melting of the ice particles induced by impurities at sub-zero temperatures.

The results reported in the preceding section concerning the dielectric behaviour of ice microcrystal dispersions obtained from the breakdown of supercooling of emulsions of NH_4Cl aqueous solutions in oil add some support to the above conclusions.

Numerous studies have been devoted to the influence of ion incorporation upon the properties of ice (see for instance Jaccard and Levi, 1961; Noll, 1969; Haltenorth and Klinger, 1969, 1977; Sakabe and others, 1970; Lafargue and Boned, 1973; Klinger, 1973; Camplin and Glen, 1973; Gross and others, 1975). Most of them consider that impurities induce strong perturbations of the ice lattice. For instance, Sakabe and others consider that one NaOH molecule could facilitate the activation of several hundred water molecules.

From comparative dielectric measurements performed on macroscopic samples of ice doped with NH_4Cl and on dispersions of microcrystals obtained from emulsions of NH_4Cl aqueous solutions in oil, Boned and others (1976) have concluded that the doping effect is enhanced in the second case. During the present study, it has been observed that, for a same value of the mass fraction of disperse microcrystals p , the intensity of the higher-temperature dielectric relaxation increases with x , the molar fraction of NH_4Cl . This result could indicate that, as the NH_4Cl incorporation increases, the number and/or size of disordered clusters increase. Moreover, the fact that the shift of T_m towards lower temperatures increases with x up to a limit which is close to the eutectic depression of the system $\text{H}_2\text{O}-\text{NH}_4\text{Cl}$ ($\Delta T_e = 15.7$ deg), could suggest that a correlation exists between the higher temperature dielectric relaxation and the ice microcrystal melting temperature.

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