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Résumé. — La dépendance en température de la constante diélectrique et de l’angle de perte ont été utilisées en parallèle avec la calorimétrie différentielle à balayage pour étudier les propriétés à basse température de microémulsions eau/huile dans l’intervalle de concentrations 0.024 $\leq C < 0.4$ (C en fraction massique) et dans la plage de températures $-150^\circ C$ à $20^\circ C$. Pour $0.222 < C < 0.4$ la constante diélectrique présente, à température décroissante, un pic aigu centré autour de $-35^\circ C$. On montre que ce dernier ne peut être exclusivement justifié en terme de polarisation interfaciale de Maxwell-Wagner. L’analyse calorimétrique permet d’obtenir les températures des différentes transitions thermodynamiques se produisant dans la microémulsion. On peut ainsi mettre en évidence une différence entre les échantillons qui présentent une fraction d’« eau libre » ($0.222 < C < 0.4$) et ceux qui n’en ont pas ($0.024 < C < 0.222$). Les variations d’enthalpie associées à la fusion de l’huile ($\Delta H_d$) et de l’eau ($\Delta H_w$) ont été déterminées en fonction de la concentration à concentrations croissantes. On a pu détecter une contribution enthalpique autour de $-10^\circ C$ due à l’eau adsorbée dans la région interphase qui se superpose à celle du dodécane ($-9.6^\circ C$). Les échantillons polydispersés ont été identifiés grâce à l’analyse de la dépendance en fréquence de la perte diélectrique de la microémulsion « liquide » à $T = 20^\circ C$. Dans les échantillons présentant une dépendance temporelle, on a pu montrer que, lors du vieillissement, la variation d’enthalpie $\Delta H_w$ associée à l’eau libre tendait vers zéro tandis que la contribution du dodécane $\Delta H_d$ augmentait. Ce phénomène a été interprété comme résultant de la formation de structures hydratées formées de 4 molécules H$_2$O sur les groupes hydrophiles des molécules tensioactives. Le processus d’hydratation se développe à tension de surface constante aux dépens de la fraction d’eau libre de la phase dispersée. Nous avons étudié l’équilibre énergétique de ce processus et déterminé l’enthalpie d’augmentation de surface associée à la formation des structures hydratées formées de 4 molécules H$_2$O.

Abstract. — The temperature dependence of the dielectric constant and loss tangent in parallel with differential scanning calorimetry (DSC) were used to study the low-temperature properties of a w/o microemulsion in the concentration interval (C, mass fraction) $0.024 \leq C < 0.4$, within the temperature range ($20^\circ C - 150^\circ C$). For $0.222 < C < 0.4$ the dielectric constant exhibits, with decreasing temperature, a sharp peak centred around $-35^\circ C$. It is shown that the latter cannot be justified exclusively in terms of a Maxwell-Wagner interfacial polarization. By means of DSC analysis the temperatures of the different thermal transitions occurring in the w/o microemulsion were obtained; a differentiation between samples that possess a « free water » fraction ($0.222 < C < 0.4$) and those that do not ($0.024 < C < 0.222$) was made; the enthalpic change associated with the melting of the dodecane-oil ($\Delta H_d$) and the water ($\Delta H_w$), contained in the samples was determined against increasing concentration. An enthalpic contribution around $-10^\circ C$ due to water adsorbed at the interphase region was detected superimposed on that of the dodecane ($-9.6^\circ C$). Polydispersed samples were identified by means of the analysis of the frequency dependence of the dielectric loss of « liquid » microemulsions at $T = 20^\circ C$. Samples exhibiting a time dependent behaviour were found in which, upon ageing, the free water $\Delta H_w$ tends to zero accompanied by the increase of the dodecane $\Delta H_d$ contribution. The phenomenon was interpreted in terms of the formation of 4 H$_2$O-molecule hydration structures on the hydrophilic groups of the surface active molecules. The hydration process develops at constant surface tension at the expenses of the free water fraction of the dispersed phase. The energy balance of the latter process was investigated and the « surface increment » enthalpy associated with the formation of the 4 H$_2$O-molecule hydrated structures was estimated.
1. Introduction.

In previous papers we reported that an optically isotropic water-in-dodecane microemulsion with hexanol and potassium oleate as surfactants, if oriented at 20 °C by a static electric field and successively solidified under the action of the same field, behaves like a «dipolar electret » [1-3].

By means of a method known in literature as Thermally Stimulated Depolarization (TSD) or Thermal Current analysis [3-5], it was shown that microemulsion samples are characterized by a «single» depolarization process whose activation energy (ξ) and relaxation time constant (τ0) can be evaluated to a high degree of accuracy since the orientation mechanism can be described by the first order relaxation kinetics:

\[
\frac{dP}{dt} = -\frac{P}{\tau} = J(T)
\]

where \( P \) is the polarization, \( \tau = \tau_0 \exp(\xi/KT) \) is the relaxation time and \( J(T) \) the depolarization current density interpreted as the rate of change of the polarization induced at a temperature \( T \) (polarizing temperature), by the electric field, with \( T = T(t) \).

It was also found that a uniform polarization, of dipolar nature, occurs in w/o microemulsions and that the space charge contributions are negligibly small [5]. Furthermore, it was demonstrated that the experimental sequence followed in the TSD measuring procedure does not modify the properties of the samples even if applied several times; provided that each time the sample under test is taken back to the temperature at which it was initially oriented.

We recall that in the TSD analysis the orientation induced in the sample by an electric field at a polarizing temperature, \( T_p \), is frozen-in by immersing the sample in liquid nitrogen, then the field is removed, the sample connected to an electrometer and the depolarization current \( J(T) \) recorded as a function of linearly increasing temperature [2, 3].

By evaluating the \( \xi \) and \( \tau \) parameters of the depolarization process obtained with repeated TSD runs, it was possible to verify that neither the imposition of the field nor the freezing and heating processes had altered the characteristics of microemulsion samples, as far as their dipole and/or charge distribution are concerned.

The thermal current analysis was applied to the isotropic w/o microemulsion (0.024 ≪ C ≪ 0.4) [2, 3], as well as to the liquid crystalline phase originating in the former upon water addition (0.5 ≪ C ≪ 0.8) [6-8] (C is the mass fraction). The polarization mechanism of the system was investigated by orienting the samples not only at 20 °C but also at several polarizing temperatures in the range \((-100, +50\, ^\circ C)\) [5, 9].

An accurate description of the temperature dependent relaxation processes occurring both in the isotropic and in the liquid crystalline states of the system was obtained and the activation energies and relaxation times (20 °C) were calculated [3, 8].

By means of: a) a study of the phase map of the system, in the temperature range \((-20, +80\, ^\circ C)\) within the concentration interval (0.024-0.95) [10]; b) the viscosity measurements vs. both concentration and temperature [10]; c) the analysis of the complex permittivity at 20 °C in the frequency range (16 Hz-50 MHz) and of the concentration dependence of \( \varepsilon' \) and \( \varepsilon'' \) at the different frequencies [8, 11, 12]; d) the study of the electro-optical properties of the system's liquid crystalline mesophases [7, 8, 13, 14], the most important features that characterize the different structures were reported and the dielectric properties associated with each of the structures were identified.

Light scattering measurements were made to ascertain that the system in the concentration interval (0.15 ≪ C ≪ 0.4) is a dispersion consisting of droplets with diameter ranging between (50-200 Å). Greater details concerning the structural investigations on the actual microemulsion, by light scattering, Raman spectroscopy and acoustic absorption can be found in references [10, 15-17]. In the present paper we describe the behaviour of the microemulsion upon solidification by paralleling low temperature dielectric measurements with Differential Scanning Calorimetry (DSC).

The study of both the permittivity (\( \varepsilon' \)) and the loss tangent (\( \varepsilon''/\varepsilon' \)) as a continuous function of decreasing temperature was undertaken with the aim of analysing the modification of the microemulsion dielectric properties during the freezing process. The DSC analysis was performed with the purpose of obtaining some experimental results dealing with basic thermodynamic properties of the microemulsion in a temperature interval not often investigated. The frequency dependence of the dielectric loss (\( \varepsilon''\delta_{\text{die}} \)) exhibited by liquid microemulsion samples (20 °C) with different water contents was also investigated in the frequency range (5 Hz-100 MHz).

The analysis of the absorption phenomena arising from Maxwell-Wagner polarization at the interface between the dispersed phase and the continuous medium of the system was used as an experimental means of verifying whether the calorimetric and low temperature dielectric results were in accordance with the properties that characterize the corresponding samples in the liquid state. The research was carried out on samples with water content (C, mass fraction), in the interval 0.024 ≪ C ≪ 0.4, within the temperature range from 20 °C down to −150 °C. Attention was focused on the « microemulsion » state of the system as well as on the early structural modifications that develop in the former at concentrations preceding the macroscopic separation of the system into two different phases [3, 10].

2. Materials and methods.

2.1 Preparation of the microemulsion. — The initial mixture of the microemulsion is composed of :
dodecane, n-hexanol and potassium oleate. The proportions by weight of the different constituents are: 58.6% dodecane, 25.6% hexanol and 15.8% K-oleate with, K-oleate/dodecane = 0.4 (g/ml) and hexanol/dodecane = 0.2 (ml/ml) [3, 18-20].

In order to solubilize the potassium oleate, 2.4% of water by weight was added to the former mixture which was thereafter kept at 20°C, sealed into a quartz bottle, for a period of one year before use [3, 5, 21].

Water-in-oil microemulsion samples were produced at 20°C by adding to the mixture very small amounts of double distilled water from a Super Q-Millipore System with a 0.2 μm Milli Stack filter.

The sample water content was expressed by the mass fraction C given by the relation: $C = \frac{\text{weight ratio (water content of the sample/water + oil))}}{0.024 \leq C < 0.4}$. The corresponding range, with C in volume fraction is $0.019 \leq C < 0.34$.

The average uncertainty on the sample water content was evaluated to be less than 1%.

2.2 DIELECTRIC MEASUREMENTS. — The dielectric study was performed following the procedure described in references [5, 11, 12], that is by measuring, as a continuous function of decreasing temperature, the impedance magnitude and the phase angle of a two electrode polarization impedance by increasing the capacitance variation technique [22-26].

The sample holder design was specifically devised in order to minimize the temperature gradient within the test fluid, to control stray field effects arising from an inhomogeneous field configuration and to reduce spurious contributions due to the polarization impedance at the interface between the electrodes and the sample surface [21-26].

The dielectric cell used was a volume independent cell with plane, parallel circular gold electrodes and variable spacing to allow corrections for electrode polarization impedance by means of the electrode distance variation technique [22-26].

The electrodes were surrounded by a thin concentric gold ring, electrically connected to the upper electrode and teflon-insulated from the bottom electrode. With this arrangement, the gold ring, being at the same potential as the upper electrode behaved as guard ring in the coaxial cylindrical geometry of the cell design. The liquid samples were confined between the electrode and the gold ring. The surface of both electrodes was roughened in order to decrease the electrode polarization impedance by increasing the capacitive contribution at the sample-electrode interface. The dielectric cell was enclosed in a stainless steel container, electrically insulated from the sample-cell, which could be directly immersed in a cryogenic and/or thermostatic bath.

The low temperature dielectric measurements were performed in the frequency range 5 Hz-500 MHz; however for a reason that will be explained in section 3.2, only the results obtained at 10 kHz will be discussed in parallel with the DSC analysis.

The sample temperature was measured with thermocouples placed inside the cell in the narrow gap between the electrode boundaries and the guard ring as well as on the upper electrode. The thermocouples were calibrated by the Italian Calibration Service, Metrological Commission of the C.N.R. Within the temperature interval from 20°C to -190°C, the sample temperature was known with an error less than ±0.05°C.

The low temperature dielectric measurements were performed by applying a temperature gradient of 0.18°C/s (10.8°C/min).

The cell constant, $C_0(F)$, that depends only on the cell geometry and on the electrode distance as well as the constant stray capacitance, $C_s(F)$, arising from the electrical connections between the sample-cell and the measuring instrument used, were both evaluated by computing the slope and the intercept of the regression line expressing the linear relationship between the measured capacitance ($C_m = C_0 \varepsilon + C_s$), and the known dielectric values of lossless standard liquids [27].

The dielectric constant ($\varepsilon'$) and the loss tangent ($\varepsilon''/\varepsilon'$) of the microemulsion were determined with an average uncertainty of 5% and 10% respectively. The reproducibility and the accuracy of the dielectric values as a function of decreasing temperature, as well as the transition temperatures of the system, were checked by measuring the temperature dependence of $\varepsilon'$ and $\varepsilon''$ of both standard calibration liquids and the pure components of the microemulsion. The calculated values were then compared with those reported in literature [27, 35]. Both $\varepsilon'$ and $\varepsilon''$ calibration values were found to be affected by a 2% error. The dielectric set up was piloted by a computer and the results assembled with the aid of a plotter. The impedance measurements were made with the Hewlett-Packard Vector Impedance Meters Models 4800A and 4815A (5 Hz-500 KHz; 0.5-100 MHz) and the LF Impedance Analyser Model 4193A (5 Hz-13 MHz). Conductance measurements were also carried out by means of a Wayne and Kerr Autobalance Bridge Model B331.

The $\varepsilon'$ and $\varepsilon''$ values were calculated with the relations given in references [11, 12, 21]. The frequency dependence of the dielectric loss ($\varepsilon''_{\text{die}}$) at 20°C of liquid microemulsion samples, was analysed in the frequency range (5 Hz-100 MHz).

The dielectric loss was obtained by subtracting from the experimentally observed absorption ($\varepsilon''_{\text{obs}}$) the dc contribution ($\varepsilon''_{\text{dc}}$) assessed from the lowest frequency measurements where, $\varepsilon''_{\text{dc}}$ was found to obey the relation $\varepsilon''_{\text{dc}} = A/\omega$, $A$ being the specific conductivity [12, 28].

The loss analysis was performed with a larger cell that allowed a variable electrode distance up to 10 mm. The sample holder geometry was, however, the same as that of the cell used for the low temperature measurements.

The $\varepsilon''_{\text{die}}$ values were determined with an average uncertainty of 8%.
2.3 ENTHALPY MEASUREMENTS. — The thermal analysis of the microemulsion was performed with a Perkin Elmer Differential Scanning Calorimeter Model DSC-1-B. The method is based upon the determination of the energy difference between the sample and a standard reference material. The instrument measures the heat-flow-rate (cal/min) by maintaining the sample and the reference isothermal to each other while they are heated or cooled with a known, linear temperature rate (°C/min). The DSC curve obtained is the recording of the heat flow rate as a function of temperature. Quantitatively the measure consists of the determination of the total heat absorbed or released during an endothermic ($\Delta H > 0$) or an exothermic ($\Delta H < 0$) process occurring, at a constant pressure, in a known weight of a given sample, over a temperature interval $\Delta T$.

The microemulsion enthalpy change ($\Delta H$) associated with any given thermal process observed, was evaluated by integrating the area of each DSC peak within the $\Delta T$ interval and assuming for the temperature at which the thermal transition takes place, the value at which the half width of the DSC peak occurs on the ascending starting branch. Such an assumption was justified with an accurate calibration procedure by measuring the transition points and the enthalpies of fusion of known weights of standard materials as well as of the highly purified components of the actual microemulsion.

The melting temperatures ($T_m$) observed and the calculated heats of fusion ($\Delta H$) were therefore compared with those reported in literature for the given substances. The agreement between the latter values and the experimentally determined ones was found to be affected by an average uncertainty lower than 1%. The reference values adopted throughout the present work for $T_m$ and $\Delta H$, are reported in table I [27-30].

The experimental relations used to evaluate $\Delta H$ are summarized in table II. Four different temperature rates were tested, namely: $2^\circ C/min$-$4^\circ C/min$-$8^\circ C/min$.

<table>
<thead>
<tr>
<th>Table I (†). — Reference melting points and enthalpy values</th>
</tr>
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<tbody>
<tr>
<td>Component</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>n-dodecane</td>
</tr>
<tr>
<td>n-hexanol</td>
</tr>
<tr>
<td>water</td>
</tr>
<tr>
<td>heavy water</td>
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</tbody>
</table>

(†) Each figure represents the mean of three independent measurements.
(°) Values found in literature; (°°) Measured values; (*) From references [27, 30]; (**) From reference [29].

<table>
<thead>
<tr>
<th>Table II. — Summary of experimental relations used to evaluate $\Delta H$</th>
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</thead>
<tbody>
<tr>
<td>1) $\Delta H_s$ : heat of fusion of a known weight of a given sample expressed in calories over grams of sample</td>
</tr>
<tr>
<td>$\Delta H_s = \frac{\text{[peak area (cm$^2$)]}.[\text{range setting (mcal.min$^{-1}$) f.s.}]</td>
</tr>
<tr>
<td>2) $\Delta H_d = (\Delta H_s)_s.[\text{(sample weight)}]/[\text{(sample dodecane content (weight)]} = \text{[cal/g] of dodecane}$</td>
</tr>
<tr>
<td>3) $\Delta H_w = (\Delta H_s)_w.[\text{(sample weight)}]/[\text{(sample water content (weight)]} = \text{[cal/g] of water}$</td>
</tr>
<tr>
<td>4) $R = \frac{\text{number of hidden water molecules}}{\text{total number of hydrophilic molecules in the sample}} = \frac{(n_w)}{n_s + n_c}$</td>
</tr>
</tbody>
</table>

Note: a) The term « hidden » is here used to indicate the amount of water that disappears upon ageing of the samples exhibiting time dependent behaviour;

b) For samples which do not exhibit any time dependent behaviour, the amount of water that is « not free » should be utilized.
and 16 °C/min. For each concentration the thermograms were made at both decreasing and increasing temperatures. The thermal results were found to be quite well reproducible in the whole concentration interval investigated except for two concentration values, \( C = 0.270 \) and \( C = 0.353 \), where time dependent phenomena were observed during the ageing of the samples. Greater details on the DSC theory and experimental procedure may be found in references [31-34].

3. Dielectric results.

3.1 Anomalous low temperature dielectric behaviour. — Depending on the sample water content, three different dielectric trends were observed.

A typical low temperature dielectric behaviour exhibited by microemulsion samples with concentration in the interval \( 0.222 \leq C \leq 0.31 \) is plotted in figure 1, curve (1) : both \( \epsilon' \) and \( \epsilon'' / \epsilon' \) increase with decreasing temperature going through a sharp maximum around \(-35 \) °C, a temperature that does not correspond to the sample transition temperature \(-11.2 \) °C.

In the range \( 0.3 \leq C \leq 0.4 \) two dielectric peaks were obtained at \(-33 \) °C and \(-15 \) °C respectively (Fig. 2). As the concentration approaches the value \( 0.4 \), the two latter peaks become squeezed together as shown in figure 3. The first peak occurs at a lower temperature and results in an exceedingly sharp spike at \(-18 \) °C while the second shifts its temperature up to \(-28 \) °C. The temperature interval within which the two dielectric transitions develop is also restricted.

Samples with very low water content in the range \( 0.024 \leq C \leq 0.222 \) did not show any peak-shaped low temperature dielectric transition (see Fig. 1, curve (2)).

3.2 Ageing effect. — At \( C = 0.270 \) and \( C = 0.353 \), time dependent phenomena were observed. That is the dielectric properties of the system were found to change upon ageing of the samples. Because of the « ageing effect », the dielectric constant and the loss tangent curves flatten and a low temperature dielectric behaviour such as that previously reported on samples with \( 0.024-0.222 \) was obtained (see Fig. 1, curve (2)). The latter result was further investigated by means of several independent experimental runs performed on samples aged respectively 3-10-15-20-30 days and even two years after their preparation.

The analysis was repeated for every concentration tested in the range 0.024-0.387. The time dependent phenomena were found to be confined in the nearest neighbourhood of the two concentrations \( C = 0.270 \) and \( C = 0.353 \). For these samples the « flat » trend shown in figure 1 by curve (2), was found to represent the final state toward which the system's dielectric properties evolve upon ageing. Aside from the above
two concentration values, reproducible results were obtained for both the single and the two-peaks shaped low temperature dielectric trends. Such a result applies not only to the 3-10-15-20-30 aged samples but also to those aged two years.

The research was carried out at several different frequencies in the interval 5 Hz-50 MHz. However, due to the ageing effect, the fixed frequency of 10 kHz was used for this particular study since it was impossible to parallel simultaneously the dielectric measurements and the thermal analysis.

3.3 DIELECTRIC LOSS OF LIQUID SAMPLES. — The frequency dependence of the dielectric loss of liquid samples at $T = 20^\circ$C is plotted in figure 4 for a few representative concentrations, one of each type of low temperature dielectric behaviour observed (flat, single-double peak shaped).

![Frequency dependence of liquid microemulsion dielectric loss ($\varepsilon_{d}$) at $T = 20^\circ$C. Each curve shows the typical behaviour of the samples in the intervals: a) 0.024 $< C < 0.22$; b) 0.22 $< C < 0.31$; c) 0.31 $< C < 0.4$. Samples exhibiting time dependent phenomena show, 3 days after their preparation, a behaviour like that of curve (2) for $C = 0.270$ and of curve (3) for $C = 0.353$. The behaviour of $\varepsilon_{d}$ against frequency of the samples with $C = 0.270$ and $C = 0.353$, measured 30 days after their preparation, is represented in figure 4 by the curve labelled « Aged ».](image)

Also the dielectric loss of two samples which exhibit time dependent phenomena were investigated, namely: $C = 0.270$ and $C = 0.353$. The measurements were performed 3 and 30 days after the preparation of the samples.

From the dielectric loss diagrams shown in figure 4 it follows that, upon water addition, superimposed on the main Maxwell-Wagner type of dispersion [35, 36] whose maximum is centred beyond the upper limit of the frequency interval examined, two other absorption processes develop: «peak A» and «peak B» centred around much lower frequencies. The «A» peak detectable at $C > 0.222$, was found to occur always at the same frequency as the concentration changes in the interval $0.222 < C < 0.4$; while the «B» peak could be observed only in the range $0.3 < C < 0.4$. The behaviour of $\varepsilon_{d}$ against frequency of the samples with $C = 0.270$ and $C = 0.353$, measured 30 days after their preparation, is represented in figure 4 by the curve labelled «Aged».

3.4 INTERFACIAL POLARIZATION. — From a purely dielectric point of view, the microemulsion can be schematized as a dispersed system in which a conducting phase is homogeneously distributed throughout an insulating medium. The dispersed phase in the actual microemulsion is a spherical droplet consisting of an interphasal chorona (amphiphiles + counte- rions), that encloses an inner water core.

It is reasonable to expect such a system to exhibit an interfacial polarization both at room temperature when it is a liquid and at low temperature when it is a solid. Interfacial polarization is also expected to arise upon decreasing temperature because of the coexistence of two phases differing in both the conductivity and the freezing point. Therefore, both the dielectric constant-peak against temperature and the increase of the loss factor, can be easily accounted for by Maxwell-Wagner phenomena [35-36]. Besides interfacial polarization, also a non homogeneous solidification of the sample upon decreasing temperature may seriously affect the system's dielectric properties, by spreading the completion of the freezing process over a considerable range of temperatures, thus giving rise to an anomalous peak at a temperature well below the sample transition temperature. However, while it is easy to justify the presence of an anomalous low temperature dielectric behaviour since we have plenty of arguments to support the interpretation that the latter is just an «apparent» anomaly linked with the particular experimental approach used, it is quite difficult, on the basis of the same arguments, to justify its absence and even more its disappearance (Aging effect). In the latter case in fact, none of the essential conditions that support interfacial polarization phenomena or spurious contributions of purely technical nature, are either absent or changed. Therefore we came to the
conclusion that the low temperature dielectric behaviour observed in the w/o microemulsion cannot be « exclusively » ascribed to a Maxwell-Wagner effect nor to a non homogeneous solidification of the samples.

3.5 DIELECTRIC LOSS ANALYSIS. — The frequency dependence of the dielectric loss of the actual microemulsion can be accounted for by assuming Sillars' model of interfacial polarization [37]. Sillars' dielectric consists of a continuous insulating medium of dielectric constant $\epsilon_1 (\sigma_1 = 0)$, in which a conducting material of dielectric constant $\epsilon_2$ and conductivity $\sigma_2$ is dispersed in the form of very small « spheroids ». These are ellipsoids with circular cross section. By introducing a shape factor $\Phi$ that depends on the eccentricity of the spheroid ($\epsilon = 3$ for the sphere), in the case of non interacting but extremely numerous spheroids, the dielectric properties of the system as a whole, may be described by an average complex permittivity $\epsilon^* = \epsilon' - j\epsilon''$. Both $\epsilon'$ and $\epsilon''$ can be a function of the complex quantities $\epsilon_1^*$ and $\epsilon_2^*$. Thus we have $\epsilon_1^* = \epsilon_1' - j\epsilon_1''$ and $\epsilon_2^* = \epsilon_2' - j\epsilon_2''$. The frequency dependence of the system's average permittivity is given by

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_1' N}{1 + (\omega \tau)^2}$$  \hspace{1cm} (2)

$$\epsilon_\infty = \frac{\epsilon_1' N \omega \tau}{1 + (\omega \tau)^2}$$  \hspace{1cm} (3)

$$\tan \delta = \frac{\epsilon_\infty}{\epsilon_\infty} = \frac{\epsilon_1' N \omega \tau}{\epsilon_\infty (1 + (\omega \tau)^2) + \epsilon_1' N}$$  \hspace{1cm} (4)

with:

$$\epsilon_\infty = \epsilon_1' \left[ \frac{1 + \Phi\Sigma(\epsilon_2' - \epsilon_1')}{\epsilon_1' (\epsilon_1 - 1) + \epsilon_2'} \right]$$  \hspace{1cm} (5)

$$\tau = \frac{\epsilon_1' (\epsilon_1 - 1) + \epsilon_2'}{\sigma_2} \text{ and } N = \frac{\Sigma^2 \Phi \epsilon_1'}{\epsilon_1' (\epsilon_1 - 1) + \epsilon_2'}$$  \hspace{1cm} (6a-b)

where:

$$\sigma_2 = \omega \epsilon_\infty; \quad \epsilon_\infty = 8.854 \times 10^{-12} \text{ Fm}.$$  \hspace{1cm} (7)

In the above relations $\Phi$ is the volume fraction of the conducting phase and $\Sigma$, the shape factor, is a coefficient that can vary from one to infinity as the spheroid shape changes from a very flat oblate to a very long prolate spheroid. From equations (1-7) it follows:

1) the relaxation time $\tau$ and the constant $N$ given by equations (6a and b), contain the shape factor, therefore both $\epsilon_1'$ and $\epsilon_2'$ increase as $\Sigma$ increases;

2) the dielectric loss $\epsilon''$ shifts its maximum to a lower frequency upon a shape change of the dispersed phase toward a more elongated configuration;

3) the loss produced by a dispersed phase of spherical shape is much less than that caused by the same amount of material distributed in the form of elongated spheroids.

4) « a dielectric that contains particles of all shapes will exhibit loss at all frequencies up to those in the neighbourhood of $1/\tau$ for spheres » (Ref. [37]);

Sillars' model can be applied to analyse the behaviour of the dielectric loss of the actual microemulsion because, under the conditions given below, the main assumptions implicit in the model may be fulfilled. That is:

a) The droplets can be schematized as in section 3.4, in terms of a conducting phase (interphasal chorona + inner water core).

b) The continuous medium can be assumed as « insulating » if all the conducting components are enclosed in the « interphasal chorona ».

c) The TSD study [2-9] has proved that microemulsion samples behave like a dipolar material for which Langevin function applies [38]. Therefore the average moment per dipole in the direction of the' electric field $E$ can be approximated by $p_0 = p^2 E/3 KT$, with $p_0$ average value of the dipole moment of each molecule, $K$ Boltzmann’s constant, $T$ absolute temperature and $pE/KT \ll 1$ (freely rotating dipoles) (see, for instance Ref. [5]).

d) Liquid microemulsion samples can be « poled » at 20 °C by means of a low level electric field (33 V/cm), hence it can be inferred that, under the action of the field, the dispersed droplets, which are not rigid spheres, undergo a deformation (different shape associated to the microemulsion droplet). The latter can be either a real shape change as that exhibited by coacervate drops, or a generalized deformation caused by migration of charges over microscopic distances as in electrets [1, 5].

e) Deformation processes in liquid oriented microemulsion samples can also be favoured by electrostriction phenomena [38].

In the case that droplets of different size were dispersed in the system, it is reasonable to suppose the larger droplets to deform more that the smaller ones. By associating a « shape factor » to the dispersed phase, according to points (2-4) and (c-d), it follows that the loss contribution due to the more elongated shape of the larger droplets can be distinguished from that caused by the smaller and therefore less deformed ones.

On the basis of Sillars' model, the complex loss spectra depicted in figure 4 by curves (2) and (3), suggest that in the concentration intervals (0.222-0.31) and (0.31-0.4) the samples may be polydispersed; that is they consist of droplets of different size. Each distribution of droplets relaxes around a mean relaxation time corresponding to the $\omega_0^{-1}$ maximum at which the different absorption processes are observed.

The main absorption at $\nu > 100$ MHz detected in each concentration tested, can be ascribed, according to point (4), to the contribution of a fraction of
particles that, having the smallest size, remain spherical and practically undeformed by the field. This is because the latter absorption occurs at the highest frequency with respect to the absorption processes exhibited by the other distributions of droplets. Therefore the loss spectrum given by curve (1) in figure 4, that characterizes the samples with concentration in the interval (0.024-0.222), can be interpreted in terms of the loss contribution due to the smallest spherical aggregates originated upon a minimal addition of water.

The disappearance of the «A» and «B» peaks upon ageing of the samples exhibiting time dependent behaviour could be ascribed to the formation, at constant concentration, of a more homogeneous type of samples with «homodispersed» droplets. On the other side the absence of any shift to lower frequencies of the main absorption maximum at \(\nu > 100\ \text{MHz}\) and the marked decrease of the dielectric loss values of aged samples can be justified, according to points (3-4), by assuming that the droplet size has become smaller than that of the non-aged samples. In fact, had the droplet size increased upon ageing, the loss maximum should have shifted to lower frequency due to the greater deformation experienced by the droplets of larger dimension. However another explanation might be possible: the decrease of \(\varepsilon'\) down to the values that characterize samples with lower concentration (see Fig. 4, curve 1), might be interpreted in terms of a decrease of the system's inner surface upon formation of «less deformable» droplets of larger dimension. The latter results can be achieved by means of an increased structural ordering within the interphasal chorona of the dispersed phase of the microemulsion.

Whether the first or the second interpretation holds cannot be justified on the basis of the dielectric experimental evidence only: the argument will be analysed further in section 4.4.

4. Enthalpy results.

4.1 THE FREE WATER CONTENT. — The thermal curves obtained by DSC analysis of the w/o microemulsion are plotted in figure 5 for two samples with \(C = 0.194\) and \(C = 0.293\). The upper curve is typical of all the samples with concentration in the interval \(0.024 < C < 0.222\); the lower of samples with water content in the range \(0.222 < C < 0.4\).

The two families of thermograms are characterized by three thermal processes at \(213\ \text{K} (-60 \degree \text{C})\), \(221\ \text{K} (-52 \degree \text{C})\) and \(263\ \text{K} (-10 \degree \text{C})\) as well as by a broad band centred around \(233\ \text{K} (-40 \degree \text{C})\) but they differ in the \(273\ \text{K} (0 \degree \text{C})\) DSC peak. The latter can be detected only on samples belonging to the concentration interval \((0.222 < C < 0.4)\).

The \(273\ \text{K}\) peak was ascribed to the fusion of a fraction of the total sample water content that, by melting at \(0 \degree \text{C}\), behaves as «free water». In order to ascertain that the above process was really due to what we called the «sample free water content», a few runs were made by adding to the initial microemulsion mixture, heavy water instead of normal water. The result shown in figure 6 proves that our
previous interpretation was correct: the D$_2$O thermal transition occurs in fact at 277 K shifted of about 4°C with respect to the H$_2$O transition.

The thermal curves were found to exhibit a reversible behaviour at both decreasing and increasing temperatures and to be temperature rate independent. At the present stage of research, on the basis of the calibration measurements we were able to identify two thermal processes among those observed in the DSC diagrams: the one occurring at 273 K and that at 263 K. The first was interpreted in terms of the fusion of the free water contained in the samples, the second to the melting of the dodecane present.

The thermal transition represented by the small « bump » at 221 K was found to occur exactly at the melting temperature of the n-hexanol. The DSC peak at 213 K (− 60°C) is hitherto not well identified. However, the shape of the peak and the evident inflection observed in the trend of the sample temperature during the dielectric measurements (see Figs. 1, 2, 3), suggests that the peak corresponds to a first-order transition.

The broad band around 233 K (− 40°C) is characterized by the following remarkable properties: a) it develops in the temperature interval within which the low temperature dielectric peak (around − 35°C) was found to occur (see Fig. 1); b) it does not depend on whether a cooling or a heating rate is applied.

The − 40°C band, initially observed during the cooling process, was at first ascribed to the presence of overcooled water; however, because of point (b), the above interpretation could not hold. As a matter of fact in the case of overcooled water, we expected the band to shift to higher temperatures upon melting of the samples.

Another possibility was therefore considered: the − 40°C band indicates that a higher order transition takes place in the (− 30 °C − 40°C) temperature interval. The latter point of view would be in accordance with: i) the shape of the thermal peak in the DSC curves; ii) the absence of any inflection in the behaviour of the sample temperature upon melting or freezing of the specimen; iii) the presence in the w/o microemulsion samples of a spontaneous polarization revealed in the corresponding temperature interval, by means of pyroelectric measurements [3, 21].

At the present stage of the research, the thermal processes occurring in the lowest temperature range (− 30 °C − 70°C), could not be analysed in detail. From a calorimetric point of view [39], considering that in the DSC the melting or freezing of the samples occurs in the absence of any impressed electric field, the low temperature processes are tentatively ascribed to the binary mixture composed of hexanol and a fraction of water, that does not melt or freeze at 0°C. Such a conclusion is based mostly on the observation that the hexanol melting point ranges between − 47°C and − 52°C (see table I). The − 60°C process could be ascribed to the solid state separation of a « mixture » since it develops at the lowest temperature with respect to the melting temperatures of all the other components of the system.

Unfortunately we could not find in the literature any reference to the low temperature phase diagram of the hexanol-water mixture. Research is in progress in order to obtain some more information about the aforementioned thermal transitions.

4.2 Aging effect. — The attention was therefore focused on the enthalpy change associated with the melting and/or the freezing of both the « free water » and the dodecane contents of the samples.

The results of the thermal analysis of microemulsion samples are plotted in figure 7 where $\Delta H_w$ and $\Delta H_d$...
are reported as a function of increasing concentration in the whole interval investigated.

The $\Delta H$ values are expressed in calories over grams of the given component in the sample, according to equations (2) and (3) of table II.

The experimental points reported in figure 7, besides those marked with numbers, represent each the mean value of 6 independent measurements. The bars are standard errors of the mean. As shown in figure 7 the enthalpy of both the dodecane and the sample free water content, exhibit a saturation trend as the system’s concentration exceeds the value $C = 0.3$.

A set of data obtained by means of one experimental DSC run, performed 3 days after the preparation of each sample, is reported in table III.

Time dependent phenomena in the samples with $C = 0.270$ and $C = 0.353$ were also observed by means of the DSC analysis in parallel with the previously described dielectric measurements.

The effect manifests itself in a rather unexpected way: upon ageing of the samples, as shown in figure 7 by the numbered points, the enthalpy change associated with the fusion of the sample free water content ($\Delta H_w$) decreases and correspondingly, that of the dodecane ($\Delta H_d$), increases. The process takes place gradually and ends with the complete disappearance of the $\Delta H_w$ contribution. With the aim of investigating in greater detail the ageing process, the calorimetric measurements were repeated at 3-7-10-15-20 and 30 days after the preparation of each sample. During this study the samples were kept at 20°C sealed into the little pans used for the DSC measurements and their weight controlled any time before and after each experimental run. In order to exclude contamination effects between the microemulsion and its container, some of the samples were also kept, always at 20°C, sealed into glass tubes and put into the DSC pans immediately before the measurements.

No attempt was made to investigate whether the conservation of the samples at a higher or lower temperature than 20°C affects the disappearance of the $\Delta H_w$ vs. time or changes the time required by the latter process to occur. The research on «ageing effect» had the only aim to follow the spontaneous evolution of the system until time independent, both calorimetric and dielectric behaviours, resulted. The time span between the different experimental runs (3-7-10-15-20-30 days) was chosen without following any particular criterion but that of the feasibility of the new set of measurements among the many in progress in the laboratory.

From the body of results shown in figure 7, it follows that when $\Delta H_w = 0$, the dodecane $\Delta H_d$ contribution appears as «more endothermic» than expected; that is, it exhibits a value which is higher than that corresponding to a sample with 100% of dodecane ($\Delta H_d^0 = 51.74$ cal/g). The more endothermic dodecane thermal process is associated not only with the absence but also with the disappearance (ageing effect) of the sample free water content. As soon as $\Delta H_w \neq 0$ and the system’s concentration exceeds $C = 0.3$, the dodecane enthalpy contribution becomes, on average, «less endothermic» than expected, while both $\Delta H_w$ and $\Delta H_d$ tend to saturate.

On the basis of the microemulsion thermal analysis, the concentration interval investigated can be divided into three main regions, namely: $0.024 \leq C \leq 0.222$; $0.222 < C < 0.31$ and $0.31 < C < 0.4$. The former is characterized by $\Delta H_d > \Delta H_w$ and $\Delta H_w = 0$;

Table III. — Differential scanning calorimetry data (*) (**)

<table>
<thead>
<tr>
<th>$C$</th>
<th>($\Delta H_1)_s$</th>
<th>($\Delta H_2)_s$</th>
<th>($\Delta H_3)_s$</th>
<th>($\Delta H_w)_s$</th>
<th>$\Delta H_{tot}$</th>
<th>$R$</th>
<th>$\Delta H_d$</th>
<th>$\Delta H_w$</th>
<th>% free H$_2$O</th>
<th>($\Delta H_1)$...</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.024</td>
<td>6.47</td>
<td>1.74</td>
<td>26.25</td>
<td>—</td>
<td>34.46</td>
<td>0.46</td>
<td>45.87</td>
<td>—</td>
<td>—</td>
<td>$\Delta H_1$ = 60°C</td>
</tr>
<tr>
<td>0.134</td>
<td>5.89</td>
<td>3.79</td>
<td>26.72</td>
<td>—</td>
<td>35.93</td>
<td>2.88</td>
<td>52.70</td>
<td>—</td>
<td>—</td>
<td>$\Delta H_2$ ($^\circ$)</td>
</tr>
<tr>
<td>0.195</td>
<td>5.93</td>
<td>3.93</td>
<td>27.72</td>
<td>—</td>
<td>37.58</td>
<td>4.82</td>
<td>54.67</td>
<td>—</td>
<td>—</td>
<td>$\Delta H_3$ = 10°C</td>
</tr>
<tr>
<td>0.222</td>
<td>5.66</td>
<td>4.82</td>
<td>26.45</td>
<td>—</td>
<td>36.93</td>
<td>5.29</td>
<td>57.98</td>
<td>—</td>
<td>—</td>
<td>$\Delta H_w$ = 0.0°C</td>
</tr>
<tr>
<td>0.247</td>
<td>5.78</td>
<td>3.67</td>
<td>22.10</td>
<td>9.43</td>
<td>40.98</td>
<td>3.19</td>
<td>50.10</td>
<td>38.04</td>
<td>47.73</td>
<td>($\Delta H_1)_s$ cal/g of sample;</td>
</tr>
<tr>
<td>0.270</td>
<td>4.96</td>
<td>4.82</td>
<td>22.10</td>
<td>13.32</td>
<td>45.20</td>
<td>2.61</td>
<td>51.64</td>
<td>49.27</td>
<td>61.82</td>
<td>$\Delta H_{tot}$ cal/g of sample;</td>
</tr>
<tr>
<td>0.271</td>
<td>5.55</td>
<td>2.84</td>
<td>26.58</td>
<td>—</td>
<td>34.97</td>
<td>6.90</td>
<td>62.21</td>
<td>—</td>
<td>—</td>
<td>$\Delta H_{tot}$ cal/g of sample;</td>
</tr>
<tr>
<td>0.293</td>
<td>5.72</td>
<td>3.40</td>
<td>18.79</td>
<td>18.36</td>
<td>46.27</td>
<td>1.66</td>
<td>45.37</td>
<td>62.42</td>
<td>78.31</td>
<td>$\Delta H_w$, cal/g of dodecane and water</td>
</tr>
<tr>
<td>0.304</td>
<td>4.48</td>
<td>2.95</td>
<td>20.68</td>
<td>16.60</td>
<td>44.71</td>
<td>2.56</td>
<td>50.69</td>
<td>54.52</td>
<td>68.40</td>
<td></td>
</tr>
<tr>
<td>0.315</td>
<td>4.98</td>
<td>3.20</td>
<td>19.40</td>
<td>16.20</td>
<td>43.78</td>
<td>2.88</td>
<td>48.33</td>
<td>51.45</td>
<td>64.55</td>
<td></td>
</tr>
<tr>
<td>0.353</td>
<td>4.20</td>
<td>2.83</td>
<td>17.76</td>
<td>17.76</td>
<td>42.55</td>
<td>3.78</td>
<td>46.83</td>
<td>50.26</td>
<td>63.06</td>
<td></td>
</tr>
<tr>
<td>0.387</td>
<td>5.45</td>
<td>3.42</td>
<td>20.43</td>
<td>16.45</td>
<td>45.76</td>
<td>5.13</td>
<td>56.89</td>
<td>42.43</td>
<td>53.23</td>
<td></td>
</tr>
</tbody>
</table>

(*) Measurements performed 3 days after the preparation of the samples;  
(**) The data refer to a single set of measurements;  
(\') $\Delta H_d$ is comprehensive of the $-40^\circ$C band and the small endotherm at the melting temperature of the n-hexanol.  
(***') Symbols, units and temperatures.
the second by $\Delta H_a < \Delta H_0^0$ and $\Delta H_w \neq 0$; the third by $\Delta H_w \neq 0$ and $\Delta H_a$ oscillating around $\Delta H_0^0$. Within the two latter regions also time dependent phenomena occurred with $\Delta H_a$ increasing to higher values than $\Delta H_0^0$ as $\Delta H_w$ tends to zero.

In the corresponding concentration intervals the dielectric properties are distinguished by: i) the "flat" low temperature dependence depicted in figure 1, curve (2) and the dielectric loss spectrum shown in figure 4, curve (1); ii) the peak shaped low temperature behaviour and the complex $\varepsilon''(\omega)$ spectrum plotted in figures 2 and 4 respectively; iii) the double-peaked low temperature dielectric transition and complex loss absorption spectrum reported in figures 3 and 4 (curve 3). In addition, the disappearance of the sample free water content as $\Delta H_w$ tends to zero, was found to parallel the vanishing of both the low temperature dielectric peaks and the dielectric relaxation processes superimposed to the main absorption occurring at a frequency higher than 100 MHz.

The aforementioned features suggest the dielectric behaviour of the system to be strictly linked with some specific property of the microemulsion which appears to manifest itself independently of the particular experimental approach used.

4.3 HYDRATION STRUCTURES. — In order to obtain more detailed information on the time dependent processes the raw data gathered during the "ageing effect" study were analysed as follows.

From the experimentally measured $\Delta H_w$ the amount of "free water" was calculated; therefore, knowing the total water content of each sample, the amount of "hidden" water could be estimated. Secondly the number of "hidden water molecules" as well as the total number of available hydrophilic groups (K-oleate + hexanol) was evaluated and the ratio, $R = n_w/(n_s + n_r)$, between the former ($n_w$) and the latter ($n_s + n_r$), obtained. The results reported in table IV, show first of all that the $R$ ratio is a small number and secondly that a change of 1-to-4 $H_2O$ molecules per hydrophilic group occurs, upon ageing, in these samples.

The above findings suggest that a process of adsorption of water molecules from the "free water" fraction of the dispersed phase toward the interphase region takes place on the hydrophilic groups of the amphiphilic molecules. The process ends with the adsorption of three water molecules per hydrophilic group.

The formation of associated structures that develop on the hydrophilic groups of surface active compounds has been extensively investigated by Steinbach and Sucker [40] who reported that a "4 $H_2O$ molecule structure" may form upon dilatation of a "1 $H_2O$ molecule structure" by adsorbing, that is, by binding three water molecules from the subphase in a water-air interface.

Every hydrated structure, at equilibrium has a well defined area requirement that depends on the size of the hydrophilic group and on the number of water molecules surrounding the latter. The area requirement ($S_4$ in $A^2$) of the "4 $H_2O$ structure" can be evaluated by means of the simple relation

$$S_4 = g + 29.2 = g + 7.3 \times n$$

Table IV. — Ageing effect.

<table>
<thead>
<tr>
<th>Days</th>
<th>Sample</th>
<th>C</th>
<th>$\Delta H_a$ (°) cal/g</th>
<th>$\Delta H_w$ (°°) cal/g</th>
<th>$%$ free water</th>
<th>$%$ hidden water</th>
<th>$R$</th>
<th>$\Delta H_{sw}$ cal/g</th>
<th>$\Delta H_{sw}$ cal/g</th>
<th>$\Delta H_{sw}$ (°°) cal/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>a</td>
<td>0.270</td>
<td>49.26</td>
<td>48.13</td>
<td>60.39</td>
<td>39.61</td>
<td>2.71</td>
<td>43.81</td>
<td>39.61</td>
<td>43.81</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.270</td>
<td>51.64</td>
<td>49.27</td>
<td>61.83</td>
<td>38.17</td>
<td>2.61</td>
<td>43.26</td>
<td>38.17</td>
<td>43.26</td>
</tr>
<tr>
<td>15</td>
<td>a</td>
<td>0.270</td>
<td>62.11</td>
<td>13.42</td>
<td>16.84</td>
<td>83.16</td>
<td>5.72</td>
<td>39.04</td>
<td>39.04</td>
<td>39.04</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.270</td>
<td>58.42</td>
<td>13.05</td>
<td>16.38</td>
<td>83.62</td>
<td>5.69</td>
<td>38.48</td>
<td>38.48</td>
<td>38.48</td>
</tr>
<tr>
<td>30</td>
<td>a</td>
<td>0.270</td>
<td>59.19</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>6.92</td>
<td>35.00</td>
<td>35.00</td>
<td>35.00</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.270</td>
<td>62.12</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>6.92</td>
<td>34.79</td>
<td>34.79</td>
<td>34.79</td>
</tr>
<tr>
<td>10</td>
<td>a</td>
<td>0.353</td>
<td>49.88</td>
<td>62.77</td>
<td>78.75</td>
<td>21.24</td>
<td>2.46</td>
<td>47.55</td>
<td>47.55</td>
<td>47.55</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.353</td>
<td>45.05</td>
<td>60.34</td>
<td>75.71</td>
<td>24.29</td>
<td>2.88</td>
<td>47.03</td>
<td>47.03</td>
<td>47.03</td>
</tr>
<tr>
<td>15</td>
<td>a</td>
<td>0.353</td>
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<td>60.25</td>
<td>75.59</td>
<td>24.41</td>
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<td>45.48</td>
<td>45.48</td>
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</tr>
<tr>
<td></td>
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<td>46.93</td>
<td>57.72</td>
<td>72.42</td>
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<td>45.47</td>
<td>45.47</td>
<td>45.47</td>
</tr>
<tr>
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<td>53.18</td>
<td>66.72</td>
<td>33.28</td>
<td>3.37</td>
<td>43.08</td>
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<tr>
<td></td>
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<td>46.83</td>
<td>50.24</td>
<td>63.03</td>
<td>36.97</td>
<td>3.73</td>
<td>42.35</td>
<td>42.35</td>
<td>42.35</td>
</tr>
</tbody>
</table>

(°) $\Delta H$: calories over grams of the component; (°°) $\Delta H'$: calories over grams of the sample. (a) Samples in DSC pans; (b) samples into glass tubes.
where, \( g(A^2) \) is the constant area of the given hydrophilic group and 29.2 \( (A^2) \) is the total area associated with \( n = 4 \text{H}_2\text{O} \) molecules, each of area 7.3 \( A^2 \).

The hydration process occurs at constant surface tension \( (\gamma = \text{constant}) \) [40]. Therefore the above mechanism allows the water interface to expand without affecting the \( \gamma \) value necessary to maintain the system's equilibrium.

In the case of the actual microemulsion, according to equation (5), since for the K-oleate \( g^b_{\text{COOH}} = 11.5 \text{A}^2 \) and for the n-hexanol \( g^b_{\text{OH}} = 6.3 \text{A}^2 \), it follows that for each one of the two latter groups, the 1 \text{H}_2\text{O} molecule structure has an area requirement \( S_{1.a} = 18.8 \text{A}^2 \) and \( S_{1.b} = 13.6 \text{A}^2 \) respectively. For \( n = 4 \), upon hydration, the area requirement increases up to \( S_{4.a} = 40.7 \text{A}^2 \) and \( S_{4.b} = 35.5 \text{A}^2 \).

The 1-to-4 \text{H}_2\text{O} hydration process could develop in the microemulsion by means of a transfer of \text{H}_2\text{O} molecules from the water bulk phase within the droplet, toward the interphase region. In this way while the area of every polar head of the amphiphiles remains constant, the interphase area stabilized by a single polar head is increased by an amount corresponding to the three water molecules that form the « surface-complex ».

From a macroscopic point of view, also an effective increase of the droplets dimensions takes place as confirmed by light scattering investigations.

In conclusion, for \( \gamma = 0 \) (Shulman line) [41] or for any \( \gamma \) value requested by the microemulsion to form, this condition is not changed by the occurrence of the above mechanism of hydration since it takes place without affecting the surface pressure, despite the increased dilution of surfactant and cosurfactant caused by water addition.

Since hydration structures occur in expanded surface phases, in the microemulsion such a process is favoured by the increase of the concentration. The above mechanism may help to keep the system's inner surface within some constant values at the expenses of the « free water » fraction of the sample. The latter observation could explain the saturation trend followed mostly by \( \Delta H_{\text{w}} \) as the concentration exceeds the value \( C = 0.3 \).

4.4 ENERGY BALANCE. — The most interesting result reported on the samples exhibiting time dependent phenomena is the gradual decrease of the sample free water content in correspondence with the increasing trend followed by the enthalpy change associated with the dodecane thermal transition.

The greater amount of heat absorbed by the dodecane « more endothermic » transition, when \( \Delta H_{\text{w}} \rightarrow 0 \), may be ascribed to the presence of an additional contribution also of endothermic nature that develops in the same temperature interval \((\approx -10^\circ\text{C})\). The overimposed thermal process could arise from the fusion of that fraction of the free water content which, by disappearing from the water bulk phase, becomes adsorbed on the hydrophilic groups to form the \text{4H}_2\text{O} molecule structure.

The formation of the above structure in the actual system could be verified by means of an energy balance estimate, as follows.

The enthalpy of association of the \text{4H}_2\text{O} molecule structure is \( \Delta H = 4.1 \text{kcal/mole} \). The process is exothermic, that is this energy is released when the change in structural configuration from 1-to-4 \text{H}_2\text{O} molecules takes place [40].

The total heat required for the fusion of each \text{H}_2\text{O} molecule of the hydrated structure may be obtained from the algebraic summation of the enthalpy of fusion of water at \(-10^\circ\text{C}\), in accordance with our previous assumption, and of the heat released by each associated water molecule that forms the \text{4H}_2\text{O} structure:

\[
\Delta H_{\text{w}}^0 = (\Delta H_{\text{w}})^{10^\circ\text{C}} - (\Delta H_{\text{w}}^0) =
\]

\[
17.77 \text{cal/g of water} \quad (6)
\]

with \((\Delta H_{\text{w}})^{10^\circ\text{C}} = 74.66 \text{cal/g} \) (see table I) and \( \Delta H_{\text{w}}^0 = 4.1/4 \text{(kcal/mole)} = 56.89 \text{cal/g} \).

The quantity given in equation (6) was called the « surface increment enthalpy ». The total work \( \Delta U_{\text{tot}} \) done to expand the water surface of the amount corresponding to the \text{4H}_2\text{O} molecule area, was therefore estimated for all the hydrophilic groups available in the given sample. We have:

\[
\Delta U_{\text{tot}} = \Delta U^* \times A \times n_i = 8.233 \times 10^{-21} \times n_i \text{(calories)} \quad (7)
\]

where:

\[
\Delta U^* = 118 \times 10^{-16} \text{erg/A}^2 \text{is the surface energy} \quad [42];
\]

\[
A = 29.2 \text{A}^2 \text{is the area requirement of the 4 \text{H}_2\text{O}}
\]

\[
n_i \text{is the number of hydrophilic groups in the sample}.
\]

The latter relation gives the total energy needed for the surface expansion. It offers an estimate between the endothermic work of expansion of the surface and the exothermic contribution arising from the formation of the \text{4H}_2\text{O} molecule structure. Since the work of expansion was found to range between 0.06-0.1 (cal) throughout the whole concentration range investigated, its contribution could be neglected because it does not significantly alter the total energy balance of the system.

Finally, by considering that the occurrence of the hydrated structures represents for the system an energy saving mechanism because of the exothermic nature of the process, it follows that the total heat absorbed during a whole DSC run by a given sample, is expected to decrease upon ageing of the same sample, if the 1-to-4 water molecule structures have really formed (see note [48]). Therefore the difference between the total DSC determined heat at an initial time \( t = t_o \) after the preparation of the sample and that measured after a time \( t_w > t_o \) at which \( \Delta H_{\text{w}} = 0 \) or
is significantly diminished, should give the total sample enthalpy decrement \( \Delta H^s_{At} \), associated with the formation of the surface complexes during the ageing process. That is:

\[
\Delta H^s_{At} = (\Delta H^s_{tot})_{t=1} - (\Delta H^s_{tot})_{t=t_w} \tag{8}
\]

During the measurements we observed that: a) an enthalpy decrement did really occur in the samples exhibiting a time dependent behaviour; b) when the \( R \) ratio increases by 3, then \( \Delta H^s_{At} \) value follows the empirical law

\[
(\Delta H^s_{At})_{exp} \approx \Delta H^s_{\beta} = \Delta H^s_e \times \alpha \text{ (cal/g of sample)} \tag{9}
\]

where, \( \alpha \) = total sample water content/sample weight, is a coefficient that gives the fraction of water available in the given weight of sample under test and, \( \Delta H^s_e \) is the surface increment enthalpy given by equation (6).

The enthalpy decrement (9) represents the total heat « released » in a sample during the formation of the 4 \( \text{H}_2\text{O} \) molecule structures and used to partly or fully compensate the endothermic heat of melting when the \( R \) ratio is increased by 3.

The result of the above calculation is shown in table IV for the samples with \( C = 0.270 \) and \( C = 0.353 \).

The hydration process was found to proceed gradually, by steps, until \( \Delta H^s_w = 0 \). The latter observation could signify that the formation of the 4 \( \text{H}_2\text{O} \) structures requires not only a certain amount of time to take place (at 20 °C), but also that it does not develop simultaneously on all the hydrophilic groups of the sample. The enthalpy decrement \( \Delta H^s_e \) calculated for the two concentrations reported on table IV are 4.8 and 6.2 (cal/g) respectively. The agreement between the experimentally measured values and the estimated ones is quite good for \( C = 0.270 \) and not as good for \( C = 0.353 \). In the latter case we did not succeed in recording the experimental values corresponding to a change of the \( R \) ratio of 3 and we also missed the measure immediately before the disappearance of the \( \Delta H^s_w \) contribution. Probably the formation of the hydrated structures follows a different kinetics in the two samples. This is to be connected to the different structures of the two samples as revealed by the dielectric loss measurements. With reference to figure 4 where we reported the frequency dependence of the dielectric loss (\( \varepsilon^\prime \)), we recall that in the case of « freshly » prepared samples (3 days), for \( C = 0.270 \) the \( \varepsilon^\prime \) spectra are characterized by two main absorption processes and by three absorption processes if \( C = 0.353 \). « Aged » samples for which \( \Delta H^s_w = 0 \), are instead distinguished by a single Maxwell-Wagner absorption centred at a frequency higher than 100 MHz.

The dielectric loss behaviour exhibited by the aged samples could be interpreted as follows: the formation of the hydrated structures is accompanied with a net decrease of the system's entropy because of both the increased order at the interphase region and the propagation of the ordering from the latter region into the bulk water subphase of the dispersed droplet. The greater structural organization within the interphaseal chorona as well as in the water core, being \( \Delta H^s_w = 0 \), may well give rise to a « less deformable » or more rigid type of dispersed phase. Thus, the two hypotheses put forward in section 3.5 to explain the dielectric loss values and the absence of any shift to a lower frequency of the only absorption process observed in the aged samples, appear to be contemporarily valid. Indeed the size of the droplets is increased; the absence of the free water content (\( \Delta H^s_w = 0 \)) shows that the water core has diminished by migration of water molecules to the interphasal region; the formation of the 4-water molecule structures leads to a more ordered and therefore less deformable chorona.

5. Discussion.

5.1 FIRST CONCENTRATION REGION. — In the interval (0.024-0.222) the DSC analysis confirms that no free water content can be detected in the system. Although a complete understanding of the system's energetics is limited by the fact that we cannot completely utilize the amount of information contained in the thermal records, the calorimetric results suggest that, in this region, the greater amount of heat absorbed in correspondence with the dodecane melting transition, may be due to the presence of an additional contribution developing in the same temperature interval (\( \approx -10 \) °C). Taking into account that the more endothermic dodecane thermal process occurs not only in parallel with the absence but also with the disappearance (ageing effect) of the sample free water content (Section 4.2), it is reasonable to ascribe this effect to the fusion of a fraction of water confined to the w/o interphase. The assumption of bound water melting around \(-10 \) °C is not in contrast with the findings reported in literature for interfacial water [43].

The dielectric constant and loss of the microemulsion follow a behaviour characterizing a dispersed system in which, according to the conclusions of section 3.5, a conducting phase is homogeneously distributed. Considering that, the maximum loss caused by the latter distribution of droplets occurs at the highest frequencies with respect to the absorption processes developing in the successive concentration regions, the former can be interpreted in terms of the loss due to the smallest spherical aggregates that can form in the lowest concentration range.

The \( R \) values calculated for the samples of this region show that the ratio between the number of water molecules and that of the hydrophilic groups of the surfactants is rather high, ranging between 3 and 5 (see table III).

The results: (a) no free water; (b) minute dimension of the aggregates; (c) presence of an interfacial fraction of bound water, are in our opinion, in very good agreement with Zulauf and Eicke [44] who
report: «with a minimal amount of water in the system the heads of the surfactants are linked together by hydrogen bonding, with water acting as a «glueing» agent», and ... «no free water can be detected in the system's aggregates».

5.2 SECOND CONCENTRATION REGION. — In the interval \((0.222 < C < 0.31)\) the calorimetric analysis demonstrates that a free water fraction can be detected in the total water content of the samples.

The low temperature dielectric study confirms that the system exhibits properties which greatly differ from those characterizing the samples of the first concentration region (see Fig. 1).

The frequency dependence of the dielectric loss supports the interpretation that the system may be polydispersed (Fig. 4, curves 2-3). The low amount of free water content in these samples, calculated from the measured \(\Delta H_{w} \), suggests that some of the droplets contain a free water core while some other do not. This is because there is not enough water to allow the formation of a continuous monolayer of surfactant molecules adsorbed at the water-oil interface, the latter being not sufficiently extended to consent such a structural organization of the hydrophilic groups.

5.3 ONSET OF MICROEMULSION. — For concentrations slightly lower than 0.3, the results \(\Delta H_{w} \approx \Delta H_{d} \) and \(\Delta H_{d} \approx \Delta H_{d}^{0}\) (see Table I and Fig. 7), show that:

(a) the same enthalpy change is associated with the above two thermal transitions; (b) the heat of fusion of the dodecane corresponds to the dodecane content of the sample. The latter observation indicates that a very significant change has occurred in the structural ordering of the dispersed phase. In fact, in this region, the properties of the system seem to depend rather strictly on the water content and even a small change in the sample concentration leads to quite different calorimetric and dielectric properties, as demonstrated by the ageing effect at \(C = 0.270\) and by the difference between the properties of the latter concentration and those of the sample with \(C = 0.271\) (see Table III and Fig. 7).

The formation of droplets exhibiting a free water content, proceeds until a concentration is reached \((C = 0.293)\) at which the \(R\) ratio becomes \(\approx 1\) (Table III). However the difference between the total sample water content and the measured fraction of free water given by \(\Delta H_{w}^{\text{tot}}\) indicates that also in this concentration range, there is still a portion of water that does not behave as free water. Therefore the droplets should consist of a continuous layer of surfactant molecules anchored to an interphasal water shell that encloses a free water core; obviously this is the microemulsion.

5.4 DIFFERENTIATED BEHAVIOUR. — Two different types of dispersions seem to develop in the concentration intervals \((0.024 < C < 0.222)\) and \((0.222 < C < 0.35)\), each being characterized by given and well reproducible both calorimetric and dielectric behaviours.

Many authors [41, 44-47] consider:

(a) the formation of a w/o interface saturated by a monolayer of surfactant molecules; 
(b) the appearance of a free water fraction as a well detectable component of the system; 
(c) the dependence of the properties of the system on the surface free energy of the surfactant monolayer, either to characterize a true w/o microemulsion or to distinguish it from a micellar solution.

The results obtained in the present paper on the samples in the above concentration ranges, appear in accordance with the aforementioned criteria of differentiation between the two types of w/o dispersions.

For the sake of clearness the two types of dispersion evidenced will be hereafter referred to as «dispersion A» \((0.024 < C < 0.222)\) and «dispersion B» \((0.222 < C < 0.35)\). The dispersion B is the microemulsion while the dispersion A, probably, corresponds to a micellar solution.

As \(C > 0.3\), the saturation trend exhibited by \(\Delta H_{w}\) demonstrates that the free water fraction of the microemulsion droplets does not become any larger. Such a result could be achieved by means of two different mechanisms, namely: (i) the system increases its degree of dispersion; (ii) a new type of polydispersity develops.

We believe the second mechanism to be more probable as the dispersed systems will always tend to minimize their free surface energy. Such a tendency is also confirmed by the values of \(\Delta H_{w}^{\text{tot}}\) measured during a whole DSC run (Table III); (see also note [48]).

Both the low temperature dielectric behaviour (Fig. 1) and the frequency dependence of the dielectric loss of liquid samples (Fig. 4), support the presence of two main distributions of droplets. On the basis of the results collected in the ageing effect study we propose that one of the above distributions consists of droplets whose interface is covered by a monolayer of surfactant molecules with 1 H\(_2\)O molecule per polar head while the other consists of droplets where hydrated structures with 4 H\(_2\)O molecules have formed on the hydrophilic groups of the surfactants. The latter conclusion is also supported by the less endothermic trend followed by \(\Delta H_{d}\) in the \(0.3 < C < 0.35\) interval. In fact, by considering the possible both negative and positive contributions to the measured enthalpic changes, always with reference to the \(\Delta H_{d}^{0}\) value, it follows that in this region two main processes can be involved, both leading to an exothermic type of contribution: (a) the formation of the 4 H\(_2\)O molecule structures; (b) the diminution of the system's internal surface. The processes being present together allow the endothermic contributions due to the melting to be more than compensated by the exothermic contributions.
5.5 Evolution Toward a Bicontinuous Structure. — Two different types of polydispersed samples are thought to develop in the interval $0.222 < C < 0.38$ of which the first is due to the coexistence, at equilibrium, of dispersion A and w/o microemulsions while the second arises from the coexistence of microemulsion droplets in equilibrium with a hydrated w/o dispersed phase. The concentration $C = 0.270$ represents, in our opinion, the upper limit of the former while, $C = 0.353$ is that of the latter.

The onset of phenomena describing the occurrence of a «bicontinuous» structure characterizes the samples with $C \geq 0.353$. Beyond 0.35 the system enters a pretransitional concentration region that precedes the «homogeneity gap» interval [3, 19] where macroscopic phase separation occurs into a w/o microemulsion and a liquid crystalline mesophase.

The DSC analysis on the isotropic phase of samples exhibiting a phase separation, has confirmed that the latter consists of a w/o microemulsion with a free water fraction also in accordance with our previous findings by light scattering investigations [10].

6. Conclusions.

From the body of the results the following conclusions and considerations can be drawn:

i) The parallel use of dielectric measurements and thermal analysis has been very fruitful as the two techniques give really complementary information. Furthermore both methods have been employed on the «real» system without simplifying modifications or disturbing labels or probes.

ii) The measured physical quantities ($\varepsilon$ and $\Delta H$) are completely general macroscopic properties of the system as a whole but their interconnections have allowed the formulation of a model of the most important region of the system i.e. the interphase. In particular, at constant concentration of other components, the proposed model is centred upon the leading role of water in determining the structure and therefore the stability of the system.

iii) The observed different behaviour of the system in the presence or in the absence of an electric field has allowed an analysis to be made of the various degrees of dispersity of the system and indicated the possibility of higher order transitions at low temperature.

iv) Beyond the possibility of distinguishing between «bound» or «free» water, the thermal curves show a continuity of behaviours characterizing the system in the whole concentration range investigated, including the initial mixture.

v) The cooling process does not alter the system and, by comparison with the measurements on liquid samples, it appears that the high temperature (liquid) configuration freezes unaltered, just like in a «tempering» process.

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References

[29] Landolt-Boernstein, in Zahlenwerte und Funktionen, 6 II Band, 4 Teil (Springer Verlag, Berlin 1961).
[48] It is worth noting that the analysis of the data based on the « total enthalpy change » associated with all the thermal processes occurring during a whole DSC run is not affected by the circumstance that the lowest part of the thermograms, in the temperature interval (−30 : −70°C, is hitherto not well understood.