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Thermally-Stimulated-Depolarization Study on the Highly Viscous Isotropic Mesophase of w/o Microemulsions (*).

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Summary. — Highly viscous, optically isotropic water-in-oil microemulsion samples (dodecane, hexanol, potassium oleate plus water) with water content in the concentration interval $0.68 \leq C < 0.8$ (C , mass fraction) were studied by means of the thermally-stimulated-depolarization (TSD) method. Different polarizing temperatures were tested from 293 K down to 188 K. Depending on the polarizing temperature, the intensity of the static electric field was increased from 33 V/cm up to 10 kV/cm. The temperature dependence of the field-induced orientation processes was investigated and the activation energy and the relaxation time of the depolarization processes that were found to follow a first-order relaxation kinetic were evaluated. The temperature domain within which the viscous, isotropic mesophase may exist was also identified. The low-temperature TSD spectra of highly viscous, isotropic microemulsion samples are characterized by a current peak at $T = 198$ K which follows a first-order kinetic and whose maximum current peak intensity is an inverse function of the polarizing temperature.

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1. - Introduction.

The system investigated is known in the literature as « water-in-oil microemulsion » (w/o). It is an optically transparent and isotropic, thermodynamically stable, liquid dispersion of water spherical droplets in an oily phase composed by 58.6% of dodecane, 25.6% of hexanol and 15.8% of potassium oleate, in the ratios K-oleate/dodecane = 0.2 and hexanol/dodecane = 0.4⁽¹⁻³⁾. This system develops a liquid crystalline (LC) phase with different mesomorphic structures of lyotropic type, for water concentrations in the interval $0.48 < C < 0.68$, where C is the weight ratio water/water + oil⁽⁴⁻⁶⁾.

The phase map of the actual system *vs.* water content, the mechanism of formation of the LC phase and the dielectric, optical, electro-optical and viscosity properties that both distinguish and characterize the system's different states as well as its mesomorphic structures have been reported in ref. (1-11).

We shall be concerned here with the thermally-stimulated-depolarization analysis (TSD)^(4,7,8) performed on samples belonging to the concentration interval in which the system exhibits a highly viscous, strongly viscoelastic, optically isotropic mesophase which occurs at the end of the birefringent LC region *before* the system inverts into an oil-in-water (o/w) type of dispersion^(3,5,12).

The present paper ends the series of works we performed on the above system with the TSD method⁽⁴⁻⁸⁾.

The whole body of results obtained represents an accurate and so far unique description of the temperature dependence of the relaxation processes occurring in w/o microemulsion samples with different w/o ratios in a concentration range that extends from the truly isotropic microemulsion region

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($0.024 \leq C < 0.31$), the « oil rich » phase, through the birefringent LC region ($0.48 \leq C < 0.68$), up to and beyond the concentration interval where the system becomes an o/w microemulsion, the « water rich » phase (^{5,6,8,11,12}).

2. - Experimental.

We recall the fundamental steps of the TSD analysis: a microemulsion sample is oriented with a static electric field (E_p) at a constant temperature T_p , which is called the polarizing temperature; after a time t_p , the sample temperature is lowered down to that of liquid nitrogen, the field-induced orientation is, therefore, « frozen-in » and the sample stays polarized (electret effect); at this point, the field is removed, the sample connected to an electrometer and the temperature of the sample raised with a constant heating rate (b). As the field-induced orientation releases, a depolarization current, $J(T)$, is measured *vs.* the linearly increasing temperature. If the system, as in our case, is a dipolar, not thermotropic material for which Langevin's expression applies, whose mechanism of polarization follows a first-order relaxation kinetic ($dP/dt = -P/\tau$), the analytical expression of the depolarization current $J(T)$ is given by

$$(1) \quad J(T) = - (P_0/\tau_0) \exp \left[\left(- \xi/KT - (b\tau_0)^{-1} \right) \int_{T_0}^T \exp [- \xi/KT] dT \right],$$

where P_0 is the initial polarization induced by E_p at T_p , b is the heating rate, T the absolute temperature, K Boltzmann's constant, ξ and τ_0 are, respectively, the activation energy and the relaxation time constant with $\tau = \tau_0 \exp [\xi/KT]$.

The values of the activation energy and of the relaxation time may, therefore, be evaluated by means of the following relation:

$$(2) \quad \ln \tau(T) = \ln \tau_0 + \xi/KT = \left(\ln \int_x^\infty J(T') dt' \right) - \ln J(T);$$

the expression on the r.h.s. in eq. (2) is derived from the integration of the experimentally measured depolarization current peak of any given orientation process. The TSD study was carried out by following the procedure described in ref. (4,6), where we also reported the experimental details as well as the theory of the method. The measurements were performed by orienting the samples at different polarizing temperatures in the interval from 293 K to 188 K. The low polarizing temperatures were obtained with a Neslab Cryocool CC-100 cold finger, controlled by an Exatrol unit and an ETP-3 temperature programmer. The freezing of the field-induced orientation and the heating processes were

the same as those applied in the previous works (4-8). In order to achieve the complete orientation of the samples, depending on T_p , the intensity of the static electric field E_p was increased from 33 V/cm up to 10 kV/cm. The sample temperature, detected with calibrated thermocouples, was known with an accuracy of ± 0.5 K, while the current values were known with an error less than 1%. The activation energy (ξ) and the relaxation time constant ($\ln \tau_0$) were calculated with an accuracy of 2%.

3. - Results.

3.1. TSD study at room temperature. - Microemulsion samples with water content in the interval $0.68 \leq C < 0.8$ appear, at room temperature (293 K), perfectly transparent and also optically isotropic if observed between two crossed polarizers with a white-light source. They are highly viscous and strongly viscoelastic. Another peculiar feature of these samples is that they exhibit a diapasonlike vibration if their container is hit with some metallic tool or simply with the finger nails. Because of the latter effect, these samples are called, in the laboratory idiom, « soundy ». The samples become soundy, on the average, 24 hours after being prepared. On soundy samples the effect disappears upon stirring, but, as soon as the stirring stops, it newly appears after

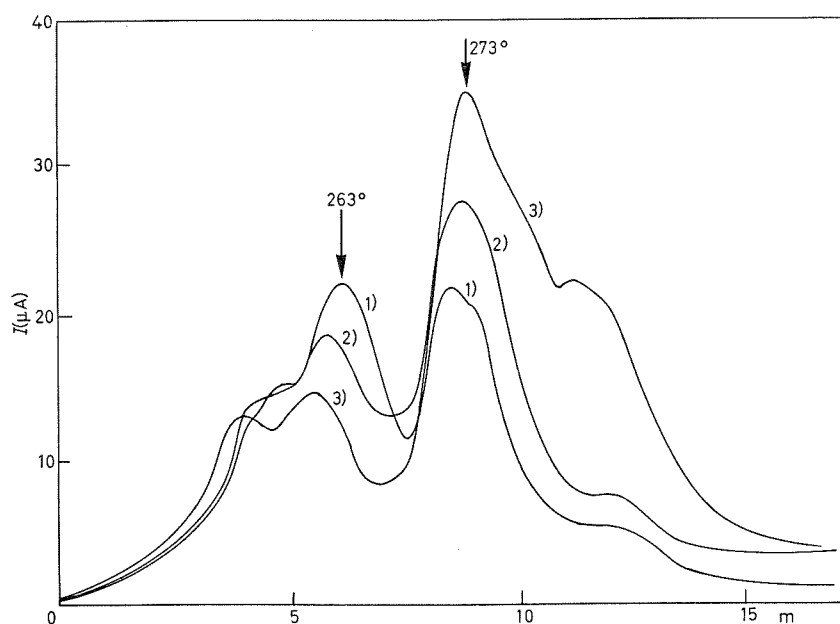


Fig. 1a. - TSD spectra of highly viscous, isotropic and « soundy » samples obtained at room temperature, $T_p = 293$ K, by applying a + 10 V, 140 kHz square wave ($E_p = 33$ V/cm): curve 1) $C = 0.752$, curve 2) $C = 0.761$, curve 3) $C = 0.767$.

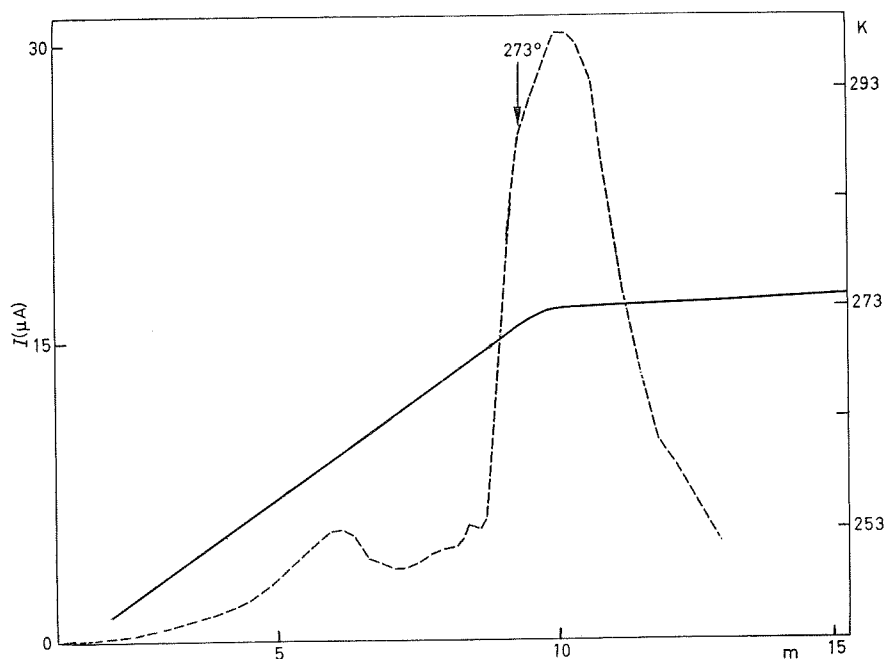


Fig. 1b. - The viscous isotropic microemulsion phase is not stable, it collapses into a transparent fluid dispersion after a period of (30÷40) days. In this picture is shown the TSD spectrum of the collapsed sample corresponding to that of curve 1) ($C = 0.752$) of the former figure, recorded 40 days later. The temperature dependence that characterizes both the highly viscous and soundy and the collapsed samples is also reported.

a few minutes. Therefore, we believe the effect to be due to some thixotropiclike organization of the swollen structural network of the system. It should be pointed out that, upon mechanical agitation, the samples do not become « liquid » as it should be if this phase were a gel. In the latter case, thixotropy is the faculty of the gel to become liquid upon mechanical agitation and to solidify again when agitation is over. Our samples maintain their highly viscous character, no matter if stirred or not. It is just the « soundy » behaviour that vanishes upon stirring and is restored at rest.

The viscous and soundy phase is not stable, it collapses into a fluid, transparent and isotropic dispersion after a period of (30÷40) days. Collapsed samples are never soundy.

A family of TSD spectra obtained by orienting at $T_p = 293$ K these viscous soundy samples is plotted in fig. 1 for three different concentrations.

In fig. 1a, the spectra are characterized by two main peaks at $T = 263$ K and $T = 273$ K, respectively. The intensity of the latter peak increases upon increasing concentration, while that of the former decreases.

The collapsed samples are instead distinguished by a TSD spectrum as

that plotted in fig. 1*b*, where the spectrum of the collapsed sample corresponding to $C = 0.752$ of fig. 1*a*, performed 40 days later, is reported.

Both the highly viscous and the corresponding collapsed samples do not follow a linear temperature dependence, as shown in fig. 1*b*. A phase transition does, in fact, occur in these samples around $T = 273$ K. Therefore, the above spectra cannot be analysed by means of the procedure reported in ref. (4,8), since the linear temperature dependence of the system is an essential prerequisite that must be fulfilled. The above spectra were obtained by applying to the samples a $+10$ V, 140 kHz square wave ($E_p = 33$ V/cm), that was found, by means of an accurate frequency-dependent dielectric analysis, to be the most suitable frequency for detecting the « viscous and soundy » characteristics of the system. The latter spectra should, therefore, not be compared with those obtained on samples belonging to the completely different phases exhibited by the system in the other concentration regions (5,6,11).

The effect of the frequency of the polarizing field on the first sample that became « soundy », being also slightly birefringent, is reported in fig. 2 ($C = 0.68$).

It is worthy of note that the temperature dependence of this sample was linear upon polarization with the 0.5 Hz E_p field, while it showed a hook inflection of the overcooled type, around 273 K, upon the orientation with the

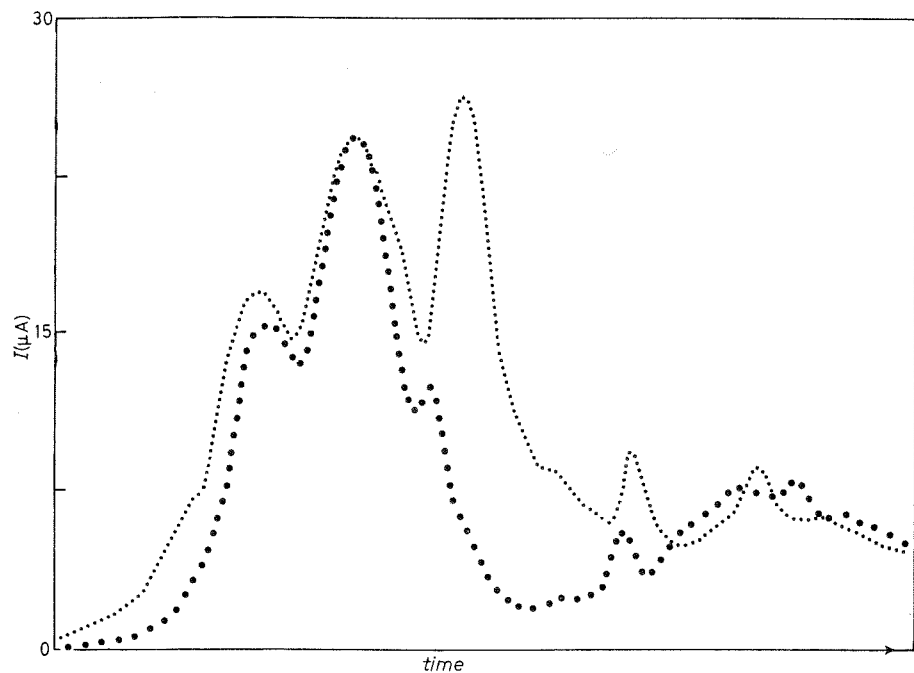


Fig. 2. — The effect of the frequency of the polarizing field E_p upon the samples with $0.68 \leq C < 0.8$. The frequency effect on the first sample that exhibited the « soundy » behaviour. $C = 0.68$, $T_p = 293$ K, $E_p = 33$ V/cm, \cdots 140 kHz, $\bullet\bullet\bullet$ 0.5 Hz.

140 kHz E_p . Since below 273 K the temperature dependence of these samples was found to be linear, we decided to study the low-temperature TSD properties of this very peculiar phase of the microemulsion.

3'2. *Low-temperature TSD study.* - The low-temperature TSD spectra of highly viscous microemulsion samples are characterized by three main features:

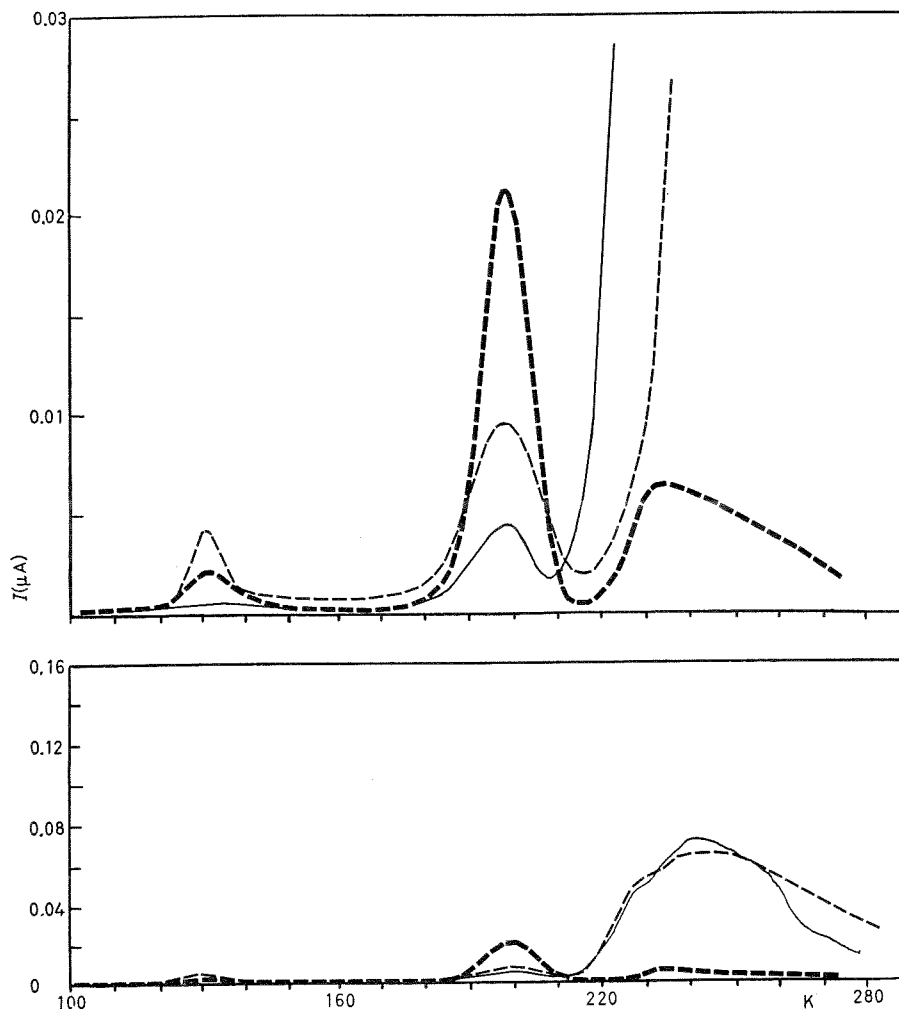


Fig. 3. - Low-temperature TSD study on a highly viscous, isotropic sample, $C = 0.752$. Top: the most remarkable feature is the depolarization process which occurs at $T = 198$ K, it follows a first-order relaxation kinetic; its maximum current peak intensity is an inverse function of the polarizing temperature. $\xi = (0.481 \pm 0.007)$ eV, $\ln \tau_0 = -26.34 \pm 0.044$. --- $T_p = 188$ K, - · - · $T_p = 196$ K, — $T_p = 207$ K. Bottom: the decrease of the 198 K current peak intensity, upon increasing T_p , corresponds to the increase of the 240 K depolarization current band.

a) A depolarization current peak at $T = 198$ K, which follows a first-order relaxation kinetic and whose maximum current peak intensity is an inverse function of the polarizing temperature (fig. 3, top).

b) A depolarization current peak at $T = 170$ K which does not follow a first-order kinetic (fig. 3, top).

c) A broad depolarization current band centred around 240 K (fig. 3, bottom). The increase of the current intensity of the latter, upon increasing T_p , was found to parallel the decrease of the 198 K current peak intensity (fig. 3, bottom).

The activation energy and the relaxation time constant of the 198 K peak, calculated by means of eq. (2), are, respectively, $\xi = (0.481 \pm 0.007)$ eV and $\ln \tau_0 = -26.34 \pm 0.044$. In the low- T_p measurements, no difference was found between the spectra performed by applying a d.c. or a 0.5 Hz signal and those obtained by orienting the samples with a 140 kHz E_p field.

A comparison of the low- T_p TSD spectra with those performed at room temperature (293 K) showed that in the latter spectra the 198 K current peak was absent.

By orienting the samples with different polarizing-field intensities, we could verify that the orientation induced in the samples at low T_p , *i.e.* below 273 K, is proportional to the intensity of the applied field E_p (fig. 4).

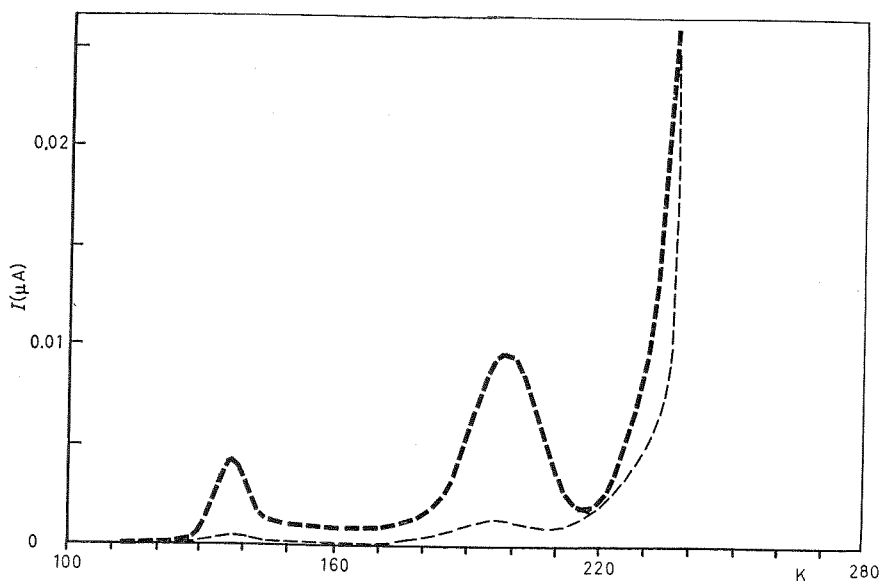


Fig. 4. - TSD spectra at two different polarizing field intensities: 1 kV/cm and 10 kV/cm, respectively. For $T_p < 273$ K, the depolarization current intensity is proportional to the impressed electric field (E_p). $T_p = 197$ K, $t_p = 10$ m, $V_p = 3$ kV (---), 300 V (- - -).

At low T_p , no difference was observed between the TSD spectra of the « soundy » samples *and those* of the corresponding collapsed ones.

We recall that the highly viscous, optically isotropic phase of the actual system follows, upon water addition, the lamellar mesophase of the w/o microemulsion LC and birefringent region ⁽¹²⁾ and precedes the concentration interval in which the system inverts into an o/w type of microemulsion.

The concentration interval of existence and the temperature domain of this phase are, respectively, $0.68 \leq C < 0.8$ and $273 \text{ K} < T < 320 \text{ K}$. The above intervals were established by means of the TSD analysis, following the procedure described in ref. (4,7,8) as well as with a careful temperature dependence study of the system's dielectric properties. The latter argument will be reported in greater details in another paper.

4. - Conclusions.

The question which arises is what kind of structure may correspond to the observed properties. At first we thought the highly viscous and « soundy » phase were a swollen lamellar unstable structure, that, *vs.* time, collapsed into an o/w type of dispersion, since the system's water content was too high to allow the lamellar mesophase to exist without modifying the proportions of

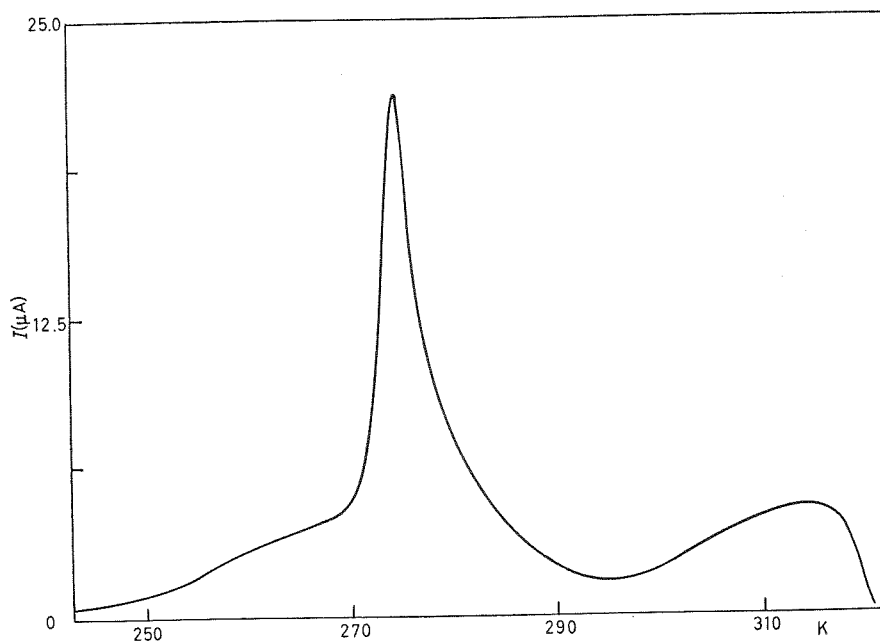


Fig. 5. - TSD spectrum of an o/w type of microemulsion. $C = 0.062$, where C = weight ratio oil/water + oil. Besides the spectrum profile, the o/w microemulsions differ from the collapsed w/o samples (see fig. 1b) in the temperature behaviour: the former exhibit a linear temperature dependence, the latter do not.

both the alcohol and the K-oleate. However, the TSD spectrum of an o/w microemulsion with $C = 0.062$, where C is the weight ratio oil/oil + water, proved that the latter system exhibits a quite distinct spectrum which is characterized by a single-peak depolarization process, as in the case of truly isotropic and perfectly fluid w/o microemulsion samples⁽⁴⁾ (fig. 5). Another macroscopic difference between the latter system and the viscous, collapsed phase is represented by their temperature dependence. Despite the fact that in the o/w samples the water content is higher than in the collapsed and viscous ones, their temperature dependence was found to be linear. Therefore, one must conclude that the viscous, collapsed phase is not an o/w microemulsion.

Their macroscopic characteristics may suggest that this phase is a cubic lyotropic mesophase of the w/o type⁽¹³⁾. Since we did not perform any X-ray study, at the present stage of the research we cannot give a definite answer to this question.

In order to understand the nature of the process that gives rise to the depolarization current peak at $T = 198$ K, in the low-temperature TSD spectra plotted in fig. 3, one must take into account that, upon water addition, the microemulsion always evolves toward a more suitable energetic structural configuration which results in the increase of the dispersed-phase dimension. The latter consists of a water core surrounded by an interphasal region of finite thickness. In such a way the system may exhibit, *vs.* increasing water content, a smaller inner surface area which may be stabilized by the given and *fixed* amount of surfactant and cosurfactant molecules available in the outer « oily » medium⁽⁵⁾.

In the actual system the cosurfactant, the potassium oleate, is a colloidal electrolyte that, as water is added, partially separates into potassium ions and long-chain ions whose action is that of compensating the electrostatic repulsion between the polar, hydrophilic heads of the amphiphilic molecules adsorbed at the water-oil interface with the hydrophobic tails pointing outward. Therefore, the dispersed phase of the microemulsion is kept stable by the action of the hexanol and the potassium oleate as well as by that of the counterions.

The structural transitions, water spheres, water channels, water and oil lamellae, are piloted by the surface-to-volume ratio of the dispersed phase and by the volume of the interphase region which represents an appreciable part of the total volume of the dispersed phase. The interfacial region, initially in a closed configuration, since the surface encloses the volume of the dispersed phase, opens up into an open layered structure as the system's water content exceeds the value $C = 0.582$ ^(5,6,11,12).

The fundamental role played by the ionic character of the cosurfactant is demonstrated by the low- T_p TSD study.

⁽¹³⁾ J. CHARVOLIN and A. TARDIEU: in *Lyotropic Liquid Crystals: Structure and Molecular Motions*, in *Liquid Crystals, Solid State Physics*, suppl. no. 14, Guest Editor L. LIEBERT (New York, N.Y., 1978), p. 209.

The behaviour of the 198 K depolarization current peak upon increasing polarizing temperature (T_p) shows that, in the temperature domain within which a given structure may exist, the counterions are obliged to fulfill their task of interface stabilizers. On the contrary, at low temperature, once the «solid» structure of the system is anyhow established, because the sample is frozen, the counterions possess a higher degree of freedom that results in the increase of the 198 K maximum current peak intensity as a function of decreasing polarizing temperatures. Therefore, the latter depolarization process is ascribed to the orientation of the system's counterions. The counterions, under the action of the polarizing field E_p , do not contribute as a mere space charge since the 198 K peak temperature does not shift by varying the sample polarizing temperature (4,7,8).

● RIASSUNTO

Mediante il metodo della polarizzazione termicamente stimolata (TSD) si sono studiate le proprietà della fase altamente viscosa e otticamente isotropa di una microemulsione composta da dodecano, esanolo, oleato di potassio e acqua, per valori del rapporto w/o nell'intervallo $0.68 \leq C < 0.8$ (C = peso del rapporto acqua/acqua + olio). I campioni sono stati orientati a diverse temperature di polarizzazione nell'intervallo da 293 K a 188 K. A seconda della temperatura di polarizzazione, l'intensità del campo elettrico statico è stata variata da 33 V/cm sino a 10 kV/cm. La dipendenza dalla temperatura dei processi di orientamento indotti dal campo nei suddetti campioni è stata quindi analizzata in dettaglio. Per i processi che seguono una cinetica di orientamento del prim'ordine si sono calcolati i valori dell'energia di attivazione e del tempo di rilassamento. È anche stato individuato il dominio di temperature entro il quale la fase altamente viscosa e isotropa della microemulsione può esistere. In questa fase gli spettri TSD a bassa temperatura di polarizzazione sono caratterizzati da un picco di depolarizzazione a $T = 198$ K che segue una cinetica del prim'ordine e la cui intensità di picco è una funzione inversa della temperatura a cui si è orientato il campione.

Исследование термически стимулированной деполяризации в сильно вязкой изотропной мезофазе микроэмульсий воды в нефти.

Резюме (*). — Используя метод термически стимулированной деполяризации, исследуются образцы сильно вязких, оптически изотропных микроэмульсий воды в нефти с концентрацией воды в интервале $0.68 \leq C < 0.8$. Поляризация образцов производилась при различных температурах от 293 K до 188 K. В зависимости от температуры поляризации интенсивность статического электрического поля увеличивалась от 33 В/см до 10 кВ/см. Исследовалась температурная зависимость процессов ориентации, индуцированных полем. Для процессов, которые описываются ориентационной кинетикой первого порядка, вычисляются значения энергии активации и времени релаксации. Указывается температурная область, внутри которой может существовать вязкая, изотропная мезофаза микроэмульсии. При низких температурах спектры термически стимулированной деполяризации для образцов сильно вязкой, изотропной микроэмульсии характеризуются пиком деполяризации при $T = 198$ K, который описывается кинетикой первого порядка, и интенсивность этого пика является обратной функцией температуры поляризации.

(*) Переведено редакцией.