Dielectric spectra of ionic water-in-oil microemulsions below percolation: Frequency dependence behavior

C. Cametti[*]

Dipartimento di Fisica, Universita' di Roma "La Sapienza" and INFM-CNR CRS-SOFT, Rome, Italy
(Received 19 November 2009; published 17 March 2010)

We have investigated the dielectric properties of water-in-oil microemulsions composed of sodium bis(2-ethyl-hexyl)sulfosuccinate, water, and decane, using radiofrequency impedance spectroscopy, below the percolation threshold, where the system behaves as surfactant-coated individual water droplets dispersed in a continuous oil phase. The analysis of the dielectric spectra has evidenced that the whole dielectric response below percolation is due to two different contributions, which give rise to two partially overlapping dielectric relaxations, approximately in the frequency range from 10 to 500 MHz. The first of these mechanisms is originated by the bulk polarization of counterions distributed in the electrical double layer of the droplet interior. The second mechanism is associated with a correlated motion of the anionic head groups SO_3^- at the surfactant-water interface. The introduction of this latter contribution allows us to justify the experimentally observed increase in the low-frequency permittivity as a function of temperature up to temperatures very close to percolation. The present study shows that deviations from the expected values on the basis of dielectric theories of heterogeneous systems (Maxwell-Wagner effect) observed when percolation is approaching can be accounted for, in a reasonable way, by the introduction of a further polarization mechanism, which involves the anionic surfactant groups. Only very close to percolation, when microemulsions undergo a scaling behavior, deviations of the permittivity (and electrical conductivity as well) are a print of the structural rearrangement of the whole system and models based on colloidal particle suspension theories fail. Even if the whole picture of the dielectric properties of microemulsion systems does not change in deep, nevertheless, the refinement introduced in this paper demonstrates how different polarization mechanisms could be simultaneously present in these rather complex systems and, above all, how the individual particle colloidal properties are maintained up to very close to the percolation threshold.

PACS number(s): 82.70.Dd

I. INTRODUCTION

Water-in-oil microemulsions are homogeneous and thermodynamically stable mixtures composed of water droplets covered by a monolayer of amphiphilic molecules (surfactants) and randomly dispersed in a continuous nonpolar medium (oil phase). Among the different microemulsion systems, the ternary mixture, consisting of a double chain anionic surfactant bis(2-ethyl-hexyl sulfosuccinate) (AOT), water, and decane, is one of the most studied systems [1–4] because of the large variety of structures the system experiences by varying simple environmental parameters, such as the temperature and the composition.

At room temperature, the mixture forms a transparent L_2 phase in which droplets are dispersed in a continuous decane phase over a wide range of volume fractions of the water droplets. This feature makes a one-phase microemulsion an appropriate colloidal model system. Molecules of AOT dissociate into anions containing a SO_3^- charged head groups and Na^+ counterions distributed into the droplet core. This is a characteristic feature of this system, where the water phase confined in spherical droplets of 50 nm in size contains a relatively high concentration of ions of the same sign (positive in this case), with marked deviation from bulk electroneutrality. For example, in a droplet of 50 nm radius, the Na^+ concentration is on the order of 1.5×10^{-2} mol/l, to be compared with a concentration of 10^{-7} mol/l of ions deriving from the dissociation of the water molecules (pH $\simeq 7$). Moreover, the thickness of the electrical double layer (measured by the Debye length) is on the order of $k_D^{-1} \simeq 2$ nm, so that the layer of the surface charge at the surfactant-water interface is strongly screened.

At higher temperature, or at higher water droplet fractional volume, these systems undergo a structural transition governed by percolation, where water droplets come in close contact and, because of spontaneous thermal fluctuations, fuse to form short-lived droplet clusters up to the formation of transient water channels arising upon opening of the surfactant monolayer.

The dielectric, and electrical conductivity as well, properties of these systems have been extensively investigated in the last two decades [5–8] and the main behavior, both below and close to the percolation, in extremely wide frequency range and over large interval of temperature and composition has been mostly well established [9]. In particular, the low-frequency dielectric response is largely due to the heterogeneous character of the system, according to the interfacial polarization of the Maxwell-Wagner effect [10].

Here, we will reexamine, in light of a unifying view, the dielectric spectra of a water-AOT-decane microemulsion below the percolation threshold, where the structural arrangement of the system is certainly simpler. On the basis of an accurate analysis of the dielectric spectra, we will analyze the different dielectric contributions that participate to the whole dielectric response. Even if these different mecha-

———
*cesare.cametti@roma1.infn.it

nisms have been known for quite some time and have been discussed and largely commented, we will show that, by combining a bulk ion polarization contribution to the one due to a correlated motion of the AOT anionic head groups, we are in the condition to describe the dielectric behavior, in light of the Maxwell-Wagner effective-medium approximation theory, up to the percolation threshold over a much more extended temperature interval than we could expect.

Our analysis, based on the decomposition of the dielectric spectra into two distinct components, evidences that those deviations from the expected values before the beginning of the percolation—which have been attributed to the beginning of the structural rearrangement—can be, on the contrary, attributed to a further dielectric interfacial polarization mechanism, involving the anionic head groups of the surfactant molecules. In any case, with the approaching of percolation, dielectric models—which consider the single water droplet as the place where dielectric polarizations take place—cannot be further applied and models based on a scaling approach [11] prevail.

II. THEORETICAL FRAMEWORK

Below the percolation onset, both the low-frequency limit of the permittivity ϵ and the dc electrical conductivity σ increase with the increase in the volume fraction Φ of the droplet phase and with the increase in the temperature T. These behaviors, as far as the electrical conductivity is concerned, are reasonably taken into account within the charge fluctuation model, according to which each droplet acquires an electric charge owing to the fluctuating exchange between the surfactant head groups at the inner droplet interface and oppositely charged counterions in the droplet core. This model, which furnishes a rather satisfactory agreement with the experimental data, yields [12,13]

$$\frac{\sigma}{\Phi} = \frac{\epsilon_0 \epsilon_m K_B T (R_d - d)}{2\pi \eta R_d^4},$$ (1)

where ϵ_m and η are the permittivity and the viscosity of the oil phase, $K_B T$ is the thermal energy, R_d is the hydrodynamic radius of the surfactant-coated water droplets, and d is the thickness of the surfactant layer.

The situation is a little bit more complex as far as the dependence on temperature T and volume fraction Φ of the static value of the permittivity ϵ is concerned. This is due to the fact that different polarization mechanisms in the different regions are simultaneously present. Among them, those related with the bulk polarization of counterions in the aqueous droplet core [14] and those related to the surface polarizability of the aqueous-surfactant interfaces [15–18] are particularly relevant and will be considered here in detail. The latter mechanism, which has been only marginally considered some time ago [19,20], is due to the presence of anionic groups derived from the dissociation of the AOT molecules that, under the influence of the electric field, undergo diffusive correlated motion relative to water droplet surface, resulting in an additional dielectric response. However, because of the structural complexity of the microemulsion

systems, other dielectric polarization mechanisms—even if less relevant—cannot be anyway excluded.

These two above-mentioned dielectric contributions fall in a relatively restricted frequency interval and are partially overlapped. We will identify the mechanism at lower frequency as the one due, besides the usual Maxwell-Wagner polarization, to the bulk ion polarization (called hereafter as β_1 dispersion) and the other at higher frequencies as the one due to the anionic head groups of the AOT molecules (and called hereafter as β_2 dispersion).

Below percolation, when the droplet-droplet interactions are negligibly small and the typical properties of the highly heterogeneous colloidal particle suspensions prevail, the whole dielectric behavior can be accounted for, at least to a first approximation, in light of the two above-mentioned contributions. In this context, Kozlovich and co-workers [14] recently developed a model which takes into account the dielectric properties of a microemulsion system, considering the contribution associated with the polarization of ions in the bulk of each water droplet besides the one associated with the heterogeneity of the system and consequently analyzed according to the Maxwell-Wagner equation for shelled colloidal particles.

On a macroscopic basis, the whole dielectric response is given by

$$\epsilon = \epsilon_{MW} + 4\pi \frac{M}{EV},$$ (2)

where ϵ_{MW} takes into account the interfacial polarization due to the Maxwell-Wagner effect and M is the total electrical dipole moment of a macroscopic volume V of the system, in the presence of an electric field E attributed to the bulk ion polarization. Following the procedure given by Kozlovich *et al.* [14], Eq. (2) can be written as

$$\frac{(\epsilon - \epsilon_{MW})(2\epsilon + \epsilon_{MW})(2\epsilon + \epsilon_w)}{\epsilon^2} = 9\Phi \frac{\langle \mu^2 \rangle}{R_d^3 k_B T},$$ (3)

where $\Phi = 4\pi N R_d^3 / 3V$ is the volume fraction of the droplets of radius R_d, $\langle \mu^2 \rangle$ is the mean-square dipole moment of the droplet, and $K_B T$ is the thermal energy. Kozlovich and co-workers [14] give the expression

$$\langle \mu^2 \rangle = \frac{32\sqrt{3}}{15} \pi e^2 \sqrt{\left(\frac{R_w^9 K_s}{A_s} \right)},$$ (4)

with A_s being the average area on the surface of the water core of radius R_w, associated with one AOT molecule, and K_s being its dissociation constant. Taking into account that, in the present case, the following approximations hold: $\epsilon \simeq \epsilon_{MW} \ll \epsilon_w$, Eq. (3) reduces to

$$\epsilon = \epsilon_{sMW} \left(1 + \frac{32\sqrt{3}}{5} \pi e^2 \Phi \frac{1}{R_d^3 K_B T \epsilon_w} \sqrt{\frac{R_w^9 K_s}{A_s}} \right).$$ (5)

As far as the interfacial polarization effect is concerned, ϵ_{sMW} can be obtained within the framework of the dielectric properties of heterogeneous colloidal particle systems in light of the Maxwell-Wagner effective-medium approximation theory [10]. For water droplets [complex dielectric con-
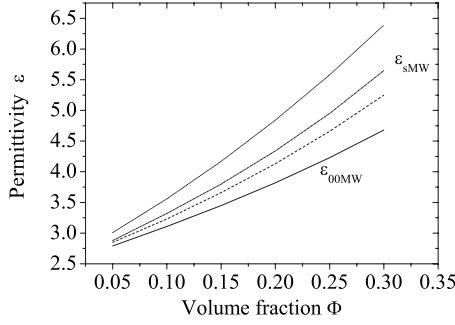
FIG. 1. Interfacial polarization effect in a microemulsion water-AOT-decane at the temperature of 15 °C as a function of the fractional volume Φ, calculated according to Eq. (6). Continuous line: the high-frequency permittivity $\epsilon_{\infty MW}$. Dotted lines: the low-frequency permittivity ϵ_{sMW} for three different values of the oil phase conductivity σ_m: $\sigma_m = 10^{-6}$ mho/m (dotted line); $\sigma_m = 10^{-7}$ mho/m (dashed line); $\sigma_m = 10^{-8}$ mho/m (dashed-dotted line). The other parameters assume the following values: $\sigma_w = 10^{-1}$ mho/m, $\epsilon_w = 81.90$, $\epsilon_m = 2.5$, $\sigma_s = 10^{-6}$ mho/m, and $\epsilon_s = 8.5$.

stant $\epsilon_w^*(\omega)$] covered by a surfactant layer [complex dielectric constant $\epsilon_s^*(\omega)$] uniformly dispersed in an oil phase [complex dielectric constant $\epsilon_m^*(\omega)$], the complex dielectric constant $\epsilon_{MW}^*(\omega)$ is given by

$$\epsilon_{MW}^*(\omega)$$
$$= \epsilon_m^*(\omega)\frac{a^*\epsilon_s^*(\omega) + 2b^*\epsilon_m^*(\omega) + 2\Phi[a^*\epsilon_s^*(\omega) - b^*\epsilon_m^*(\omega)]}{a^*\epsilon_s^*(\omega) + 2b^*\epsilon_m^*(\omega) - \Phi[a^*\epsilon_s^*(\omega) - b^*\epsilon_m^*(\omega)]},$$
$$(6)$$

where

$$a^* = (1 + 2v)\epsilon_w^*(\omega) + 2(1 - v)\epsilon_s^*(\omega),$$

$$b^* = (1 - v)\epsilon_w^*(\omega) + (2 + v)\epsilon_s^*(\omega), \qquad (7)$$

with $v = [R_w/(R_w+d)]^3 = (R_w/R_d)^3$. In the present case, the complex dielectric constants of the media involved reduce to

$$\epsilon_s^*(\omega) = \epsilon_s, \quad \epsilon_m^*(\omega) = \epsilon_m, \quad \epsilon_w^*(\omega) = \epsilon_w + \frac{\sigma_w}{i\epsilon_0\omega}, \qquad (8)$$

since the electrical conductivities of the oil phase and of the surfactant layer can be assumed to be negligibly small in comparison with the electrical conductivity of the aqueous particle core. From Eq. (6), the low-frequency limit ϵ_{sMW} and the high-frequency limit $\epsilon_{\infty MW}$ can be easily obtained as

$$\epsilon_{sMW} = \lim_{\omega \to 0} \mathrm{Re}[\epsilon_{MW}^*(\omega)],$$

$$\epsilon_{\infty MW} = \lim_{\omega \to \infty} \mathrm{Re}[\epsilon_{MW}^*(\omega)]. \qquad (9)$$

In the following, numerical calculations will be carried out assuming $\epsilon_s = 8.5$ [21] and $\epsilon_m = 2.5$. As can be seen in Fig. 1, for a water-in-oil microemulsion, the dielectric increment due to the interfacial polarization, according to the Maxwell-Wagner effect, is relatively small (contrarily to what happens in oil-in-water microemulsion, where this effect dominates).

However, the whole measured dielectric effect is small to the same extent (on the order of tens of dielectric units), so that the interfacial polarization effect cannot be neglected.

The further contribution that we have to consider—and that we called β_2 dispersion, generally occurring at higher frequencies—is due to polarization associated with the collective motion of the anionic AOT head groups with respect to the apolar part of the surfactant molecules, at the water droplet interface. This model has been originally introduced by Pottel *et al.* [15] to take into account the intermediate dispersion observed in aqueous colloidal phospholipid solutions and is based on the diffuse thermal rotational motion of the zwitterionic phosphorylcholine groups around axes perpendicular to the permanent electric dipole moment.

Although this model has been developed for aqueous colloidal solutions of zwitterionic phospholipids and applied to different phospholipid-water systems [16–18], it can be easily extended to a microemulsion system replacing each dipole moment of the zwitterionic molecule with the anionic group of the surfactant which undergoes a diffusive motion relative to its hydrophobic part. This motion, restricted to a circular path of radius ξ and characterized by a mobility u, may impart an apparent fluctuating electrical dipole to the whole water droplet which, in turn, gives rise to a dielectric dispersion.

Following the model derived by Pottel *et al.* [15], the expected dielectric increment $\Delta\epsilon$ and the corresponding relaxation frequency ν are given by

$$\Delta\epsilon = \frac{9\Phi\Delta\epsilon_z}{(2 + \Phi)^2\left(1 + \dfrac{1 - \Phi}{2 + \Phi}\dfrac{\epsilon_{sMW}}{\epsilon_m}\right)\left(1 + \dfrac{1 - \Phi}{2 + \Phi}\dfrac{\epsilon_{sMW} + \Delta\epsilon_z}{\epsilon_m}\right)},$$
$$(10)$$

$$\nu_z = \frac{uK_BT\left(1 + \dfrac{1 - \Phi}{2 + \Phi}\dfrac{\epsilon_{sMW} + \Delta\epsilon_z}{\epsilon_m}\right)}{2\pi\xi^2\left(1 + \dfrac{1 - \Phi}{2 + \Phi}\dfrac{\epsilon_{sMW}}{\epsilon_m}\right)}, \qquad (11)$$

where $\Delta\epsilon_z$ is given by

$$\Delta\epsilon_z = \frac{4\pi ne^2\xi^2g}{R_wk_BT}. \qquad (12)$$

Here, n is the number of the anionic head groups per droplet surface unit area, ξ is the displacement of the anionic group in the polar part of the AOT molecule, and finally g is the orientational correlation factor which denotes the extension of the dielectric-in-phase domain of n correlated anionic groups. The relevant quantities of this model are the product $g\xi^2$, which is related to the dielectric strength $\Delta\epsilon_z$, and the ratio u/ξ^2 of the anion mobility u to the square of the displacement ξ, which is related to the relaxation frequency ν_z. This polarization mechanism, which is strongly dependent on temperature, manifests only at higher temperatures before the beginning of the percolation, when—owing to the structural rearrangement of the system—each water droplet loses its individuality. In this context, the product $g\xi^2$ defines the static surface polarizability and strongly depends on the re-

orientational motion of the anionic charges. Analogously, the ratio u/ξ^2 defines the dynamics of the surface polarizability.

III. EXPERIMENT

A. Materials

The surfactant AOT was obtained from Fluka (purum) and was used without further purification. n decane was from Sigma Chem. Co. and was of the highest grade commercially available. De-ionized water with electrical conductivity of 1 μmho/cm was used throughout the experiments. Micro-emulsions of different water contents were freshly prepared by dissolving under constant stirring appropriate weights of water to portions of a mixture containing AOT and decane.

The water-to-surfactant molar ratio was maintained constant to the value W=[water]/[surfactant]=40.8, so that the particle radius is 53.4 Å [22]. The volume fraction of the dispersed phase was obtained from weight measurements of the different components used to prepare the microemulsion, considering the density of AOT as 1.14 g/ml and assuming an ideal mixing behavior. Within the temperature range and the volume fractions investigated, the microemulsions remained transparent and no phase transition was noticed visually.

B. Dielectric measurements

The dielectric measurements were carried out by means of two impedance analyzers (Hewlett-Packard) over the frequency range from 40 Hz to 110 MHz (model 4294A) and over the frequency range from 1 MHz to 2 GHz (model 4291A). The dielectric cell consists of a short section of a cylindrical coaxial cable connected to the meter by means of a precision APC-7 connector, whose electrical constants have been determined by a calibration procedure with standard liquids of known conductivity and dielectric constant. Details of the dielectric cell and the calibration procedure have been reported elsewhere [23,24]. The dielectric measurements have been carried out in the temperature range from 5 to 45 °C, within 0.1 °C.

IV. RESULTS AND DISCUSSION

We have measured the dielectric spectra of water-AOT-decane microemulsions of different volume fractions (Φ in the range from 0.10 to 0.35), over the frequency range from 1 kHz to 2 GHz, in the temperature interval from 5 to 45 °C. Typical dielectric spectra, as far as the permittivity $\epsilon'(\omega)$ and the electrical conductivity $\sigma(\omega)$ are concerned, are shown in Figs. 2 and 3. The spectra refer in particular to a microemulsion system with Φ=0.30 in the temperature interval from 10 to 28 °C. As expected, with the increase in temperature T and the volume fraction Φ, the system approaches the percolation condition with the formation of larger and larger droplet clusters whose size expands to occupy the whole space. A typical behavior observed close to the percolation threshold is shown in Fig. 4, where the two well-known effects, concerning the maximum of the permittivity ϵ close to the percolation and the sharp increase in the electrical con-
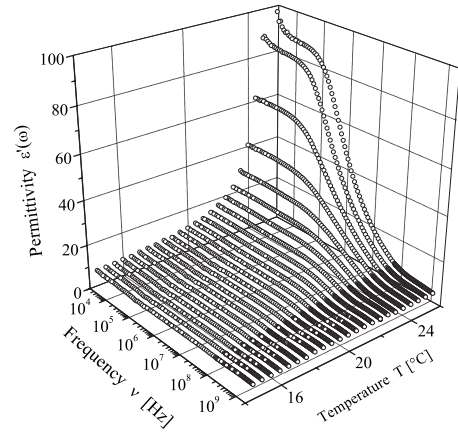

FIG. 2. Typical dielectric spectra of water-AOT-decane microemulsions (volume fraction Φ=0.30) in the frequency range from 1 kHz to 2 GHz at different temperatures between 15 and 24 °C, below the percolation threshold.

ductivity σ over more than five orders of magnitude, are clearly evidenced.

Once we have verified that the system behaves accordingly to what we expect as far as the percolation is concerned, we address attention to its behavior well below percolation (where the system is considered as a collection of noninteracting colloidal particles) and we analyze in more detail the frequency dependence of the permittivity $\epsilon'(\omega)$.

To be more precise, we will refer to dielectric spectra of water-AOT-decane microemulsion at a volume fraction Φ =0.30, some of which—at some selected temperatures below percolation—are shown in Fig. 2. At lower temperatures, let us say up to 15 °C, the spectra are well described by a Cole-Cole relaxation function,

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau)^\gamma} + \frac{\sigma_0}{i\omega\epsilon_0}, \tag{13}$$

where $\Delta\epsilon$ and $\tau=1/2\pi\nu$ are the dielectric increment and the relaxation time (ν is the relaxation frequency) of the relax-
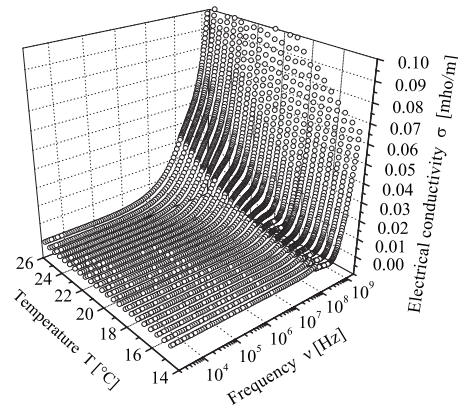

FIG. 3. Typical electrical conductivity spectra of water-AOT-decane microemulsions (volume fraction Φ=0.30) in the frequency range from 1 kHz to 2 GHz at different temperatures between 15 and 24 °C, below the percolation threshold.
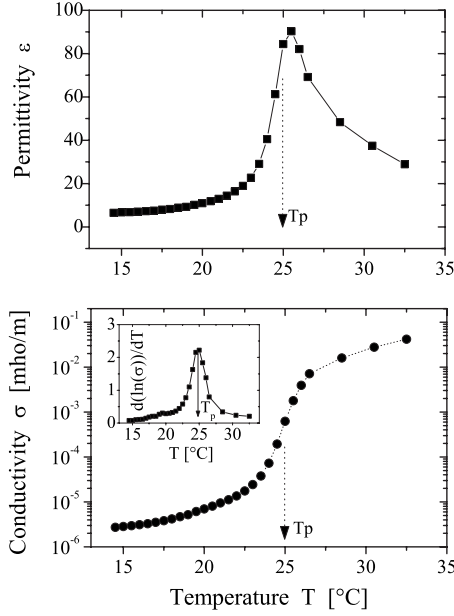
FIG. 4. Upper panel: the low-frequency limit ϵ of the permittivity $\epsilon'(\omega)$ as a function of temperature for a microemulsion water-AOT-decane at a volume fraction $\Phi = 0.30$. The percolation occurs at the temperature $T_p = 25$ °C, in correspondence of which there is the maximum in the permittivity ϵ_s. Bottom panel: the low-frequency electrical conductivity σ as a function of temperature with the typical sigmoidal behavior due to percolation. The inset shows $d\ln(\sigma)/dT$ as a function of temperature. The maximum identifies the percolation temperature T_p.

ation process, γ takes into account the spread of the relaxation times, σ_0 is the dc electrical conductivity, ϵ_∞ is the high-frequency limit of the permittivity, ϵ_0 is the dielectric constant of free space, and ω is the angular frequency of the applied electric field.

The dielectric parameters $\Delta\epsilon$, ν, and γ have been derived from the fitting of Eq. (13) by means of a nonlinear least-squares minimization to the experimental data. In particular, we obtain values of γ within the range 0.9–0.95, suggesting that the spectra approach simple Debye relaxation functions, excluding the possibility that the spectra, in these conditions, could result from the overlapping of different relaxation processes.

As the temperature is increased, let us say from 15 to 23 °C, which is still lower than the percolation threshold, the above picture becomes a little more complicated. The values of γ decreases up to 0.5–0.6, suggesting that the spectra result from the partial overlapping of more than one dielectric relaxation. Consequently, we have analyzed the data by means of a relaxation function given by

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau)^\gamma} + \frac{\sigma_0}{i\omega\epsilon_0} + \frac{\Delta\epsilon_z}{1 + (i\omega\tau_z)}, \quad (14)$$

where, to the Cole-Cole function [Eq. (13)], we have added a further dielectric contribution described by a Debye relaxation function, characterized by a dielectric strength $\Delta\epsilon_z$ and a relaxation frequency $\nu_z = 1/2\pi\tau_z$.
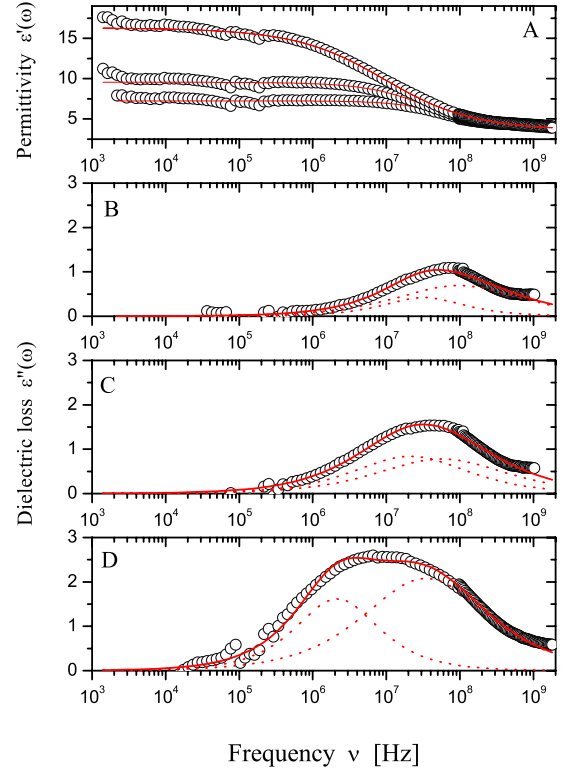

FIG. 5. (Color online) Dielectric spectra of water-AOT-decane microemulsions (volume fraction $\Phi = 0.10$) as a function of frequency, at three different temperatures below percolation threshold. (A) The permittivity $\epsilon'(\omega)$ at 17.0, 18.0, and 19.0 °C (from bottom to top). The full lines represent the calculated values according to the relaxation function of Eq. (14). (B) The dielectric loss $\epsilon''(\omega)$ at the temperature of 17.0 °C. (C) The dielectric loss $\epsilon''(\omega)$ at the temperature of 18.0 °C. (D) The dielectric loss $\epsilon''(\omega)$ at the temperature of 19.0 °C. In each panel, the full lines represent the calculated values according to the relaxation function of Eq. (14). The dotted lines represent the contribution of the processes according to which the decomposition of the spectra has been carried out.

The attribution of the two different dispersions to different molecular mechanisms is quite straightaway, in light of the above stated theoretical model, with the dispersion at lower frequency being attributed to concomitant effect of the interfacial polarization (Maxwell-Wagner effect) and of the ion polarization in the water core, according to the model of Kozlovich et al. [14] (the one we have named β_1 dispersion) and the dispersion at higher frequency being attributed to correlated movement of AOT anions at the water-surfactant interface (the one named as β_2 dispersion).

It is worth noting that we can observe this latter contribution only at higher temperatures, even if still below percolation. The reason for this is twofold. First, at lower temperature, for water-in-oil microemulsion, the total dielectric strength is rather small, on the order of a few dielectric units, and the interfacial polarization (Maxwell-Wagner effect) dominates. In these conditions, it is rather difficult, from an experimental point of view, to point out a composite spectrum evidencing two different components. Second, the mobility u of the AOT anions is strongly dependent on the temperature and the whole effect manifests only at the higher temperatures.
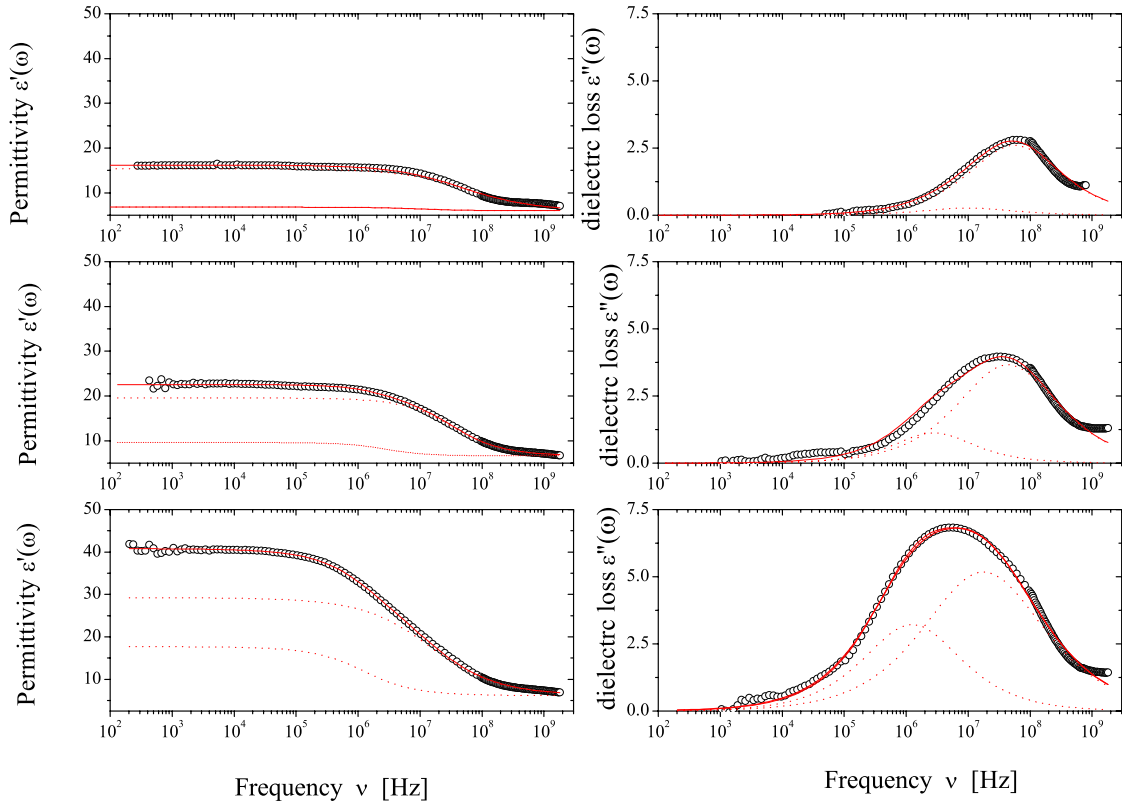
FIG. 6. (Color online) Dielectric spectra of water-AOT-decane microemulsions (volume fraction $\Phi=0.30$) as a function of frequency, at three different temperatures below percolation threshold. On the left and from top to bottom: the permittivity $\epsilon'(\omega)$ at 22.0, 23.0, and 24.0 °C. On the right and from top to bottom: the dielectric loss $\epsilon''(\omega)$ at the temperatures of 22.0, 23.0, and 24.0 °C. In each panel, the full lines represent the calculated values according to the relaxation function of Eq. (14). The dotted lines represent the contribution of the two processes, according to which the decomposition of the spectra has been carried out.

Two typical examples of the decomposition of the dielectric spectra which illustrate the presence of two distinct relaxation regions are shown in Figs. 5 and 6, for microemulsions with $\Phi=0.10$ and 0.30, respectively. Similar results have been found for the other volume fractions investigated. As we have already noted, the low-frequency contribution is assigned to both the ion and Maxwell-Wagner polarization, whereas the high-frequency contribution is assigned to the AOT polarization.

Figure 7 shows a typical result where we present the values of the limiting permittivities at low and high frequencies derived from the fitting of Eq. (13) to the experimental data, compared with those calculated taking into account the ion polarization inside the water core (Feldman model [Eq. (5)]) and the interfacial polarization due to the Maxwell-Wagner effect. As can be seen, a reasonably good agreement is obtained only at lower temperatures, where the dielectric spectra can be appropriately described by a single Cole-Cole relaxation function [Eq. (13)]. Deviations from the measured values occur exactly when the dielectric spectra must be analyzed on the basis of Eq. (14) and a further relaxation process appears.

It must be noted that these deviations cannot be attributed to the beginning of the percolation that occurs at temperatures above those at which these deviations are noticed. In this range of temperatures (up to about 23 °C, for the microemulsion with $\Phi=0.30$), the microemulsion consists of a col-

lection of isolated surfactant-coated water droplets, as also confirmed by dynamic light scattering measurements (data not shown).

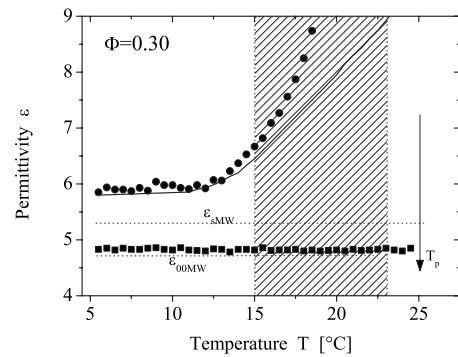These discrepancies are accounted for, in a very reasonable way, if we add the second contribution we are dealing

FIG. 7. The limiting values of the permittivity ϵ as a function of temperature T for a microemulsion water-AOT-decane at a volume fraction $\Phi=0.30$. (●): low-frequency permittivity; (■): high-frequency permittivity. The dotted lines represent the calculated values ϵ_{sMW} and $\epsilon_{\infty MW}$ according to the Maxwell-Wagner interfacial polarization effect [Eqs. (6) and (9)]. The full line represents the calculated values according to Eq. (5). Deviations marked by the shadow area occur as the temperature increases, approaching the percolation threshold, marked by the arrow.
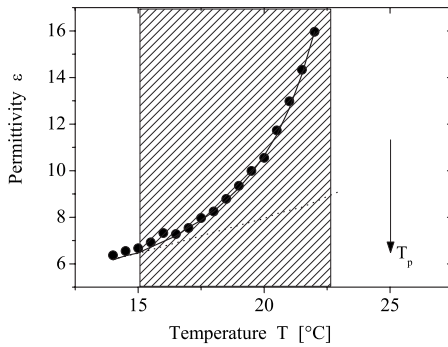
FIG. 8. The permittivity ϵ of a water-AOT-decane microemulsion at $\Phi = 0.30$ as a function of temperature in the temperature range where the Feldman model [Eq. (5)] fails (dashed region). Dotted lines represent the calculated values according to Eq. (5) (Feldman model), whereas the full line represents the values when the further contribution due to the AOT contribution [Eq. (10)] is added. The agreement is extended toward higher temperatures, approaching the percolation temperature, marked by the arrow.

with (the β_2 dispersion), considering the surface polarization of the anionic SO_3^- head groups of the AOT surfactants. Figure 8 shows the region where deviations occur on the basis of Eq. (5) (β_1 dispersion) and illustrates how these deviations disappear when the second contribution (β_2 dispersion) is appropriately taken into account. In this way, the disagreement observed on the basis of the only β_1 dispersion (dashed region in Fig. 7) vanishes when the β_2 dispersion is added (dashed region in Fig. 8).

Further evidence of the above quoted picture derives from the temperature dependence of the relaxation frequency of the high-frequency dielectric contribution (β_2 dispersion). In Fig. 9, we compare the observed value of the relaxation frequency ν_z derived from the decomposition of the dielectric spectra in the temperature interval below percolation, where deviations occur with the ones calculated according to Eq. (11), considering appropriate values for the anion mobility of u and a displacement ξ. It must be noted that the decomposition of the dielectric spectra according to Eq. (14) yields the values of the model parameters $g\xi^2$ and u/ξ^2. We obtain values in the range $g\xi^2 = 0.5 - 0.9$ nm^2 and u/ξ^2 in the range between 0.5×10^{20} and 3×10^{20} s/g nm^2. The diffusion path length ξ of the anionic groups is not known, so the correlation factor g and the mobility u cannot be explicitly evaluated. However, if ξ is assumed as the length of the stretched SO_3^- group, the minimum value of g and the maximum value of u can be calculated. We obtain values of $g \simeq 3$ and u on the order of 10^6 s/g. With these values, as can be seen in Fig. 8, a very satisfactory agreement with the experimental data is reached.
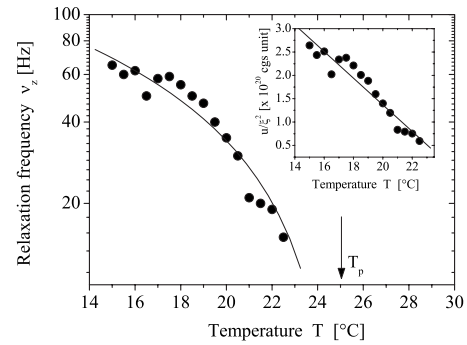

FIG. 9. The relaxation frequency ν_z of the higher relaxation process (β_2 dispersion) as a function of temperature below the percolation threshold, for a water-AOT-decane microemulsion at $\Phi = 0.30$. The full line represents the calculated values according to Eq. (11), with values of the parameters u/ξ^2 shown in the inset. The arrow marks the percolation temperature.

V. CONCLUSIONS

We have investigated the dielectric properties of a typical three-component water-in-oil microemulsion over an extended frequency range, at different temperatures, well below the percolation threshold. We suggest that the deviations of the low-frequency dielectric response from the expected behavior, observed in water-in-oil microemulsion systems as the temperature is increased, cannot be attributed—as done so far—to the beginning of the percolation threshold. On the contrary, these deviations can be considered as a print of the presence of a further dielectric polarization mechanism, occurring at the water-surfactant interface and associated with correlated motion of the anionic group of the ionized surfactant molecule.

Although this dielectric contribution was proposed more than two decades ago by Pottel *et al.* [15] to justify the intermediate dielectric relaxation in phospholipid vesicle suspension, it has never been applied, in a systematic way, to a quite different heterogeneous system, such as a microemulsion, where the role of the dipole moment of the zwitterionic lipid is replaced with the anionic group of the ionic surfactant. In the past, we had tried to apply this model to microemulsion systems, confining our investigation to the high-frequency region of the dielectric spectrum. Now, we re-examine this aspect in a more exhaustive approach, in light of the dielectric theory of colloidal heterogeneous systems.

Our results suggest that a modified dielectric theory which also includes a further polarization at the water-surfactant interface, attributable to the ionized AOT surfactant molecules, holds in a more extended temperature range than what has been believed so far and that deviations occur only very close to the percolation, when the water droplets lose their individuality and bigger and bigger clusters form.

[1] T. De and A. Maitra, Adv. Colloid Interface Sci. **59**, 95 (1995).

[2] S. H. Chen and J. S. Huang, Phys. Rev. Lett. **55**, 1888 (1985).

[3] C. Cametti, P. Codastefano, P. Tartaglia, J. Rouch, and S. H. Chen, Phys. Rev. Lett. **64**, 1461 (1990).

[4] H. Kataoka, T. Eguchi, H. Masui, K. Miyakubo, H. Nakayama, and N. Nakamura, J. Phys. Chem. B **107**, 12542 (2003).

[5] J. Peyrelasse, M. Moha-Ouchane, and C. Boned, Phys. Rev. A **38**, 904 (1988).

[6] J. Peyrelasse and C. Boned, J. Phys. Chem. **89**, 370 (1985).

[7] K. Asami, Langmuir **21**, 9032 (2005).

[8] T. Spehr, B. Frick, I. Grillo, P. Falus, M. Muller, and B. Stuhn, Phys. Rev. E **79**, 031404 (2009).

[9] F. Bordi and C. Cametti, in *Ion Transport and Electrical Conductivity in Heterogeneous Systems: The Case of Microemulsions*, Interfacial Dynamics, edited by N. Kallay (M. Dekker, New York, 2000).

[10] M. Clausse, in *Dielectric Properties of Emulsions and Related Systems*, Encyclopedia of Emulsion Technology, edited by P. Becher (Dekker, New York, 1983), Vol. 1.

[11] Z. Saidi, C. Mathew, J. Peryelasse, and C. Boned, Phys. Rev. A **42**, 872 (1990).

[12] H. F. Eicke, M. Borkovec, and B. Das-Gupta, J. Phys. Chem. **93**, 314 (1989).

[13] N. Kallay and A. Chittofrati, J. Phys. Chem. **94**, 4755 (1990).

[14] N. Kozlovich, A. Puzenko, Y. Alexandrov, and Y. Feldman, Phys. Rev. E **58**, 2179 (1998).

[15] R. Pottel, K. D. Gopel, R. Henze, U. Kaatze, and V. Uhlendorf, Biophys. Chem. **19**, 233 (1984).

[16] U. Kaatze, S. C. Muller, and H. Eibl, Chem. Phys. Lipids **27**, 263 (1980).

[17] U. Kaatze, R. Henze, and R. Pottel, Chem. Phys. Lipids **25**, 149 (1979).

[18] R. Henze, Chem. Phys. Lipids **27**, 165 (1980).

[19] C. Cametti, P. Codastefano, and P. Tartaglia, Ber. Bunsenges. Phys. Chem. **94**, 1499 (1990).

[20] C. Cametti, P. Codastefano, and P. Tartaglia, J. Non-Cryst. Solids **131-133**, 187 (1991).

[21] M. Belletete, M. Lachapelle, and G. Durocher, J. Phys. Chem. **94**, 5337 (1990).

[22] S. H. Chen and M. Koltarchyk, in *The physics of micelles, vesicles and amhiphiles*, edited by V. Degiorgio and M. Corti (North-Holland, Amsterdam, 1985).

[23] F. Bordi, C. Cametti, and T. Gili, Bioelectrochemistry **54**, 53 (2001).

[24] F. Bordi, C. Cametti, A. Motta, and G. Paradossi, J. Phys. Chem. B **103**, 5092 (1999).