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Dielectric Behavior of Highly Conducting Perfluoropolyether Water-in-Oil Microemulsions

Marcello Carlà, Cecilia M. C. Gambi,
Maria Grazia Giri, Loris Pieraccini,
Donatella Senatra

Department of Physics, University of Florence, Italy

Alba Chittofrati and Aldo Sanguineti

Ausimont R & D Center, Colloid Laboratory, Bollate,
Italy

ABSTRACT

The dielectric and conductive properties of a new ternary water-in-oil microemulsion consisting of perfluoropolyether (PFPE) oil, PFPE surfactant and water, were investigated by an impedance analysis technique in the frequency range of 5 Hz to 100 MHz. The trend of both the electrical conductivity and the static permittivity was analyzed as a function of the temperature in the interval from -10 to $+40^{\circ}\text{C}$. Maxwell-Wagner relaxation phenomena in the MHz range and a percolative transition, of dynamic type against temperature, were observed.

1. INTRODUCTION

THE present paper deals with the analysis of the dielectric and the conductive behavior of perfluoropolyether (PFPE) water-in-oil (w/o) microemulsions.

A w/o microemulsion is a thermodynamically stable single-phase fluid containing two bulk, insoluble, liquids such as water and hydrocarbon and one or more surface active agents (surfactant). In w/o microemulsions the water is dispersed in a continuous oily phase in the form of very small spherical droplets, 3 to 10 nm in diameter, stabilized by a surfactant shell, see Figure 1 [1, 2].

Since 1943 microemulsions have been on the market as: self polishing floor waxes, cutting oils, detergents and dry cleaning products and polymer lattices for paints. These

systems are largely used in enhanced oil recovery processes (the so-called tertiary oil recovery). The mechanism of formation of amphiphile association structures, microemulsions, micellar solutions as well as their lyotropic mesophases, offer basic support in the field of biophysical (phospholipid bilayers and vesicles) and biomedical (anesthesia) research as well as of agronomical applications [2-4].

The actual microemulsion is a ternary system composed of PFPE-oil (O), PFPE-surfactant (S) and water (W). The chemical composition of the perfluoropolyether compounds is reported in [5, 6].

The phase diagram of the system, at $T = 20^{\circ}\text{C}$, is shown in Figure 2. The continuous line indicates the

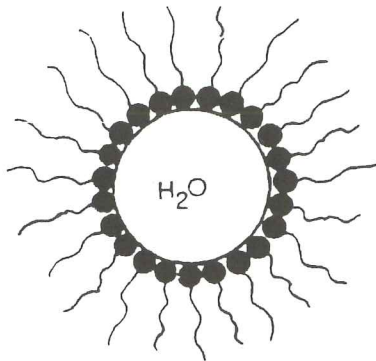


Figure 1.

Water-in-oil microemulsion droplet (schematized).

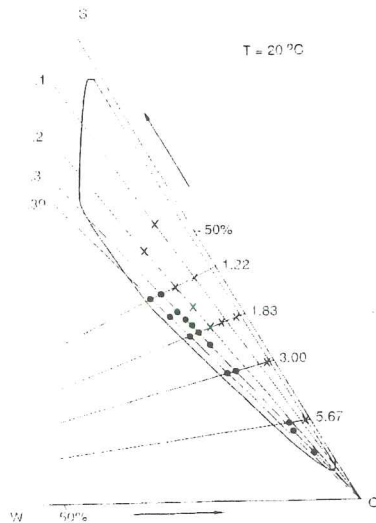


Figure 2.

Phase diagram of Perfluoropolyether oil (O), perfluoropolyether surfactant (S) and water (W) ternary system (fractions by weight).

domain within which fluid, homogeneous and transparent monophasic samples are found for water contents < 17.7% and surfactant-to-oil weight ratio (S/O) in the range 0.05 to 0.48.

PFPE w/o microemulsions of the monophasic domain are characterized by an electrical conductivity that increases from 0.05 to 0.4 S/m as the oil-to-surfactant (O/S) weight ratio decreases from 5.67 to 1.22 [7].

Structural analysis by light scattering [7, 8] and NMR [9] studies, have confirmed the existence of w/o structural aggregates consisting of droplets with dimensions in the range 3 to 6 nm.

2. METHODS

The monophasic region depicted in Figure 2 was investigated first by moving along lines that are the loci of samples characterized by the same water-to-surfactant

(W/S) weight ratio and, secondly, by crossing the above region also along lines with a constant S/O weight ratio.

The dielectric study was carried out in the frequency range 5 Hz to 100 MHz. Two Hewlett-Packard impedance analyzers were used, Model 4192, in the low frequency and Model 4815 A in the radio frequency range. In both cases the measured parameters were the impedance magnitude $|Z|$ (Ω), and the phase angle φ of the dielectric cell filled with the sample [10, 11]. Two sample holders, both temperature controlled, were built specifically devised to suite the prerequisite of low frequency and radio frequency measurements. A four-terminal cell, with rectangular gold electrodes at fixed distance, was used with the LF instrument and a cylindrical volume independent cell, with stainless steel plane parallel electrodes and variable spacing, was adopted in connection with the RF instrument. In both cases roughened electrodes were used to minimize polarization impedance. Pressure-induced effects were also prevented.

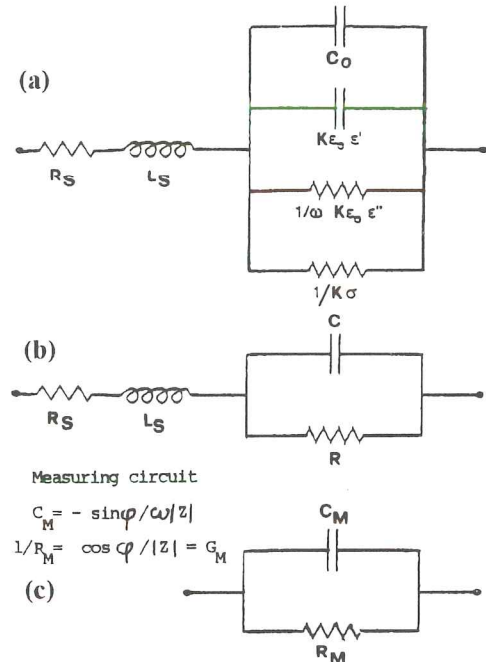


Figure 3.

Equivalent circuit of the system sample holder plus PFPE microemulsion sample.

A great deal of effort was devoted to define the appropriate equivalent circuit of the system measuring cell with microemulsion sample, because of the high electrical conductivity of the system under test. The equivalent circuit of the cell system is shown in Figure 3.

The cell constants and the values of the parasitic elements obtained through a careful calibration are reported in Table 1. The set of equations used in the calibration

procedure and the dielectric analysis is given in Appendix A. Greater details on the measuring technique and the calibration method can be found in [11].

Table 1.

Values of parasitic elements and cell constants obtained by calibration.

	LF cell	RF cell
C_o (pF)	2.2 ± 0.3	6.80 ± 0.04
L_s (nH)	128.0 ± 0.5	30.6 ± 0.5
R_s (Ω)	0.110 ± 0.007	0.60 ± 0.01
k (10^{-2} m)	4.96 ± 0.03	36.1 ± 0.1

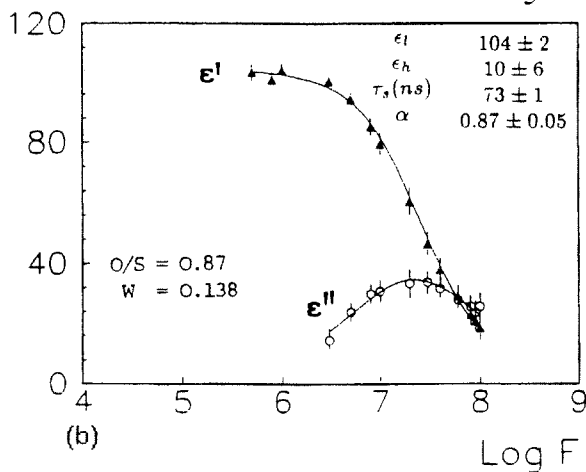
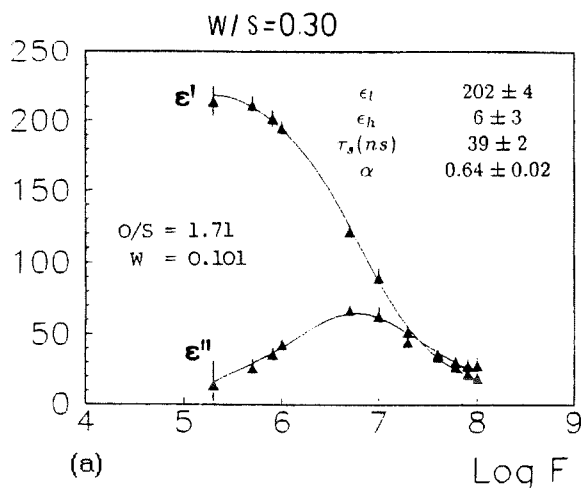


Figure 4.

Maxwell-Wagner relaxation of PFPE w/o microemulsions along the line $W/S = 0.3$. Triangles and circles: experimental points; continuous line: best fit calculated curves. The values of the parameters of Equation (5) of Appendix A, are also given.

3. RESULTS

The results of the dielectric analysis are summarized in Figures 4 to 6 for microemulsion samples with constant

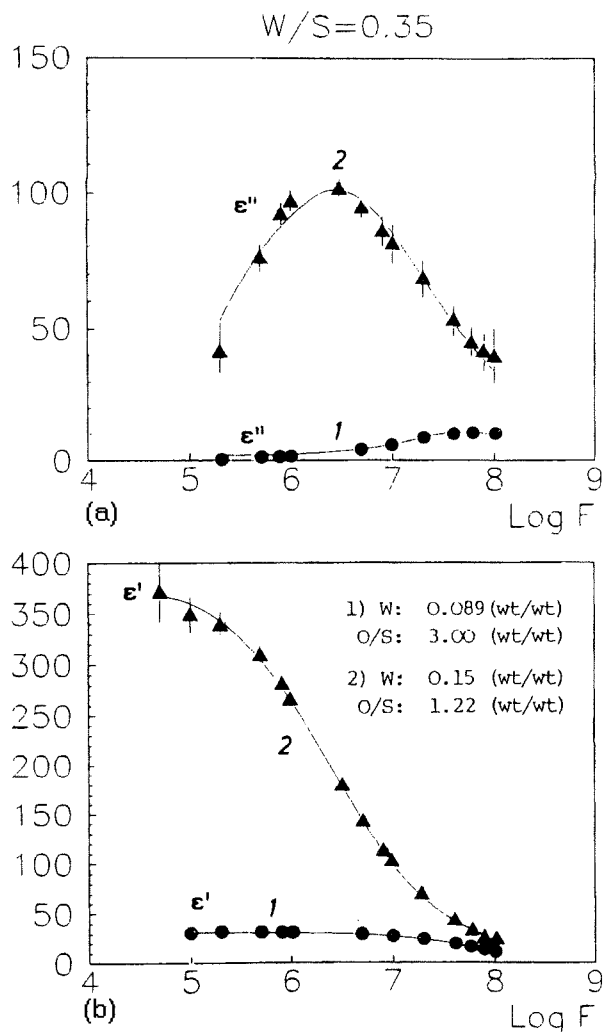


Figure 5.

Maxwell-Wagner relaxation of samples along the line $W/S = 0.35$. Note the frequency shift of the relaxation maxima.

W/S weight ratio and different O/S ratios as well as water content. The experimental ϵ' and ϵ'' data, at each frequency, were obtained from Equations 1 and 2 of Appendix A. The continuous lines of Figures 4 to 6 represent the functions $\epsilon'(f)$ and $\epsilon''(f)$ (Equation (5) of Table 2), as obtained by the fit program Minuit (CERN Library). Samples with composition in the range $W/S < 0.3$ and $O/S \leq 5.6$, do not exhibit any dielectric relaxation in the frequency interval investigated. Moreover, the electric conductivity vs. temperature does not show any peculiar trend, but a smooth increase of about one order of magnitude as the temperature is raised from -10 to $+40^\circ\text{C}$, as shown in Figure 7. Samples with composition in the range $0.2 < W/S < 0.39$ and $5.6 < O/S < 0.9$, display a Maxwell-Wagner relaxation due to interfacial polarization in a frequency range typical of w/o microemulsions.

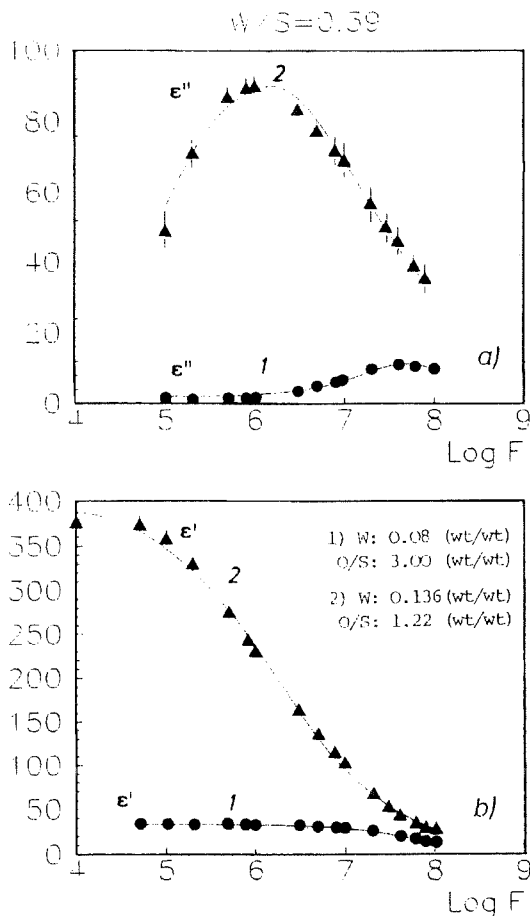


Figure 6.

The same as in Figure 5, along the line $W/S = 0.39$.

The values of the dielectric parameters can be interpreted by means of the Hanai model for a statistical distribution of non-interacting spherical particles in an insulating liquid matrix, the oil, with a very low volume fraction of the dispersed phase [12], only for very dilute w/o systems with a volume fraction of conducting medium < 0.1 .

Moving along lines of constant W/S ratio toward a more concentrated region, large ϵ' and ϵ'' values and a frequency shift of the relaxation maxima can be observed (Figures 5 to 6); moreover a variation of several orders of magnitude in the electrical conductivity vs. temperature was recorded (Figure 8).

The findings of large dielectric values, the conductivity behavior and the frequency shifts of the relaxation maxima, are highly suggestive of a percolation type of transition [13].

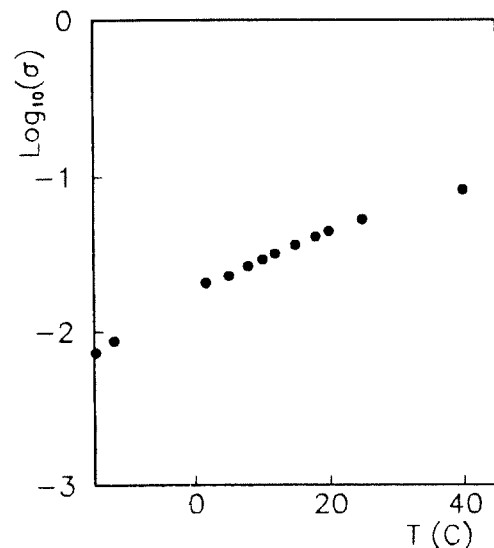


Figure 7.

Electrical conductivity vs. temperature. Sample composition 1.9% of water, $W/S = 0.13$ and $O/S = 5.67$.

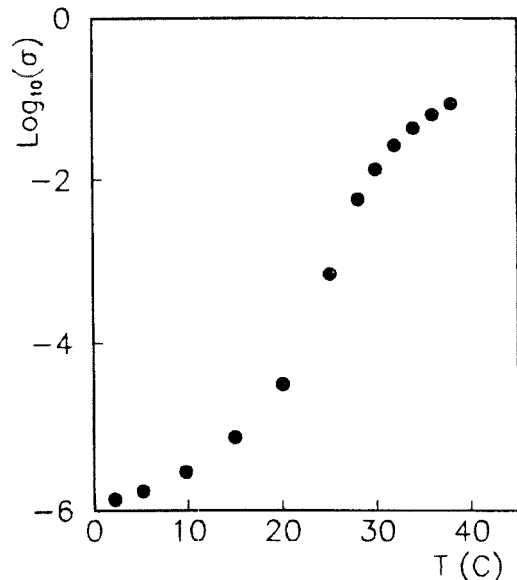


Figure 8.

Behavior of the electrical conductivity against temperature for a sample of composition. $W/S = 0.39$, $O/S = 3$ and 8.9% of water by weight.

4. PERCOLATION STUDY AND DISCUSSION

Specifically, percolation implies fluid that passes through an inert random medium: 'water percolates through sand'. Broadbent and Hammersley (1954) [14] introduced for the first time lattice models to describe the flow of a fluid through a static medium and showed that no fluid will flow if the concentration of the active medium, the

fluid, is smaller than some non-zero value. The latter was called 'percolation threshold' and the phenomenon 'percolation transition'. Later on, the percolation theory was used conceptually and theoretically to describe also the mechanism of electrical conduction and transport properties in inhomogeneous media, both solid (metal-non metal) and liquid, (two-phase systems in which one phase is electrically conducting and the other one is either nonconducting or possesses a much lower degree of electrical conductivity) [13, 14].

In order to have a percolative behavior, the main point consists in the degree of connectedness of the conducting phase through the system's insulating phase. The latter depends on the concentration, by volume, of the conductive components which, in turn, depends on the dimension of the conducting regions with respect to the mean free path of the charge carriers as well as on the presence of short range interactions between the aggregates.

Short range interactions play a fundamental role in fluid inhomogeneous systems because they favor the clustering process via the aggregation of dispersed particles of the conducting phase, thus leading to the formation of a continuous cluster connecting the system.

Whether or not a system percolates can be established only by verifying if the experimental data follow the scaling laws that describe percolative processes as obtained from phase transition and critical phenomena theories [15].

Efros and Shklovskii [14] have also shown that a sharp increase in the static permittivity $\epsilon_s(\omega, \Phi)$ near the percolation threshold Φ_p can be observed at any non-zero frequency if only the dc conductivity of the dielectric medium is much lower than that of the conducting phase. As the volume fraction of the conducting phase of the two-component system approaches the percolation threshold, ϵ_s should exhibit a symmetric peak-shaped trend. Moreover, the above authors emphasized that at $\Phi = \Phi_p$, both the conductivity and the static permittivity constant are functions of the volume fraction of the conducting phase as well as of the frequency.

The theoretically expected behavior of $\sigma(\Phi)$ and $\epsilon_s(\Phi)$ vs. the volume fraction of the conducting phase, is reported in Figures 9(a) and (b). For w/o microemulsions it has been shown that these systems can go through a percolation transition either when the volume fraction Φ or the temperature T is varied [16, 18]. If the percolative volume fraction (Φ_p) is a slowly varying function of the temperature, then both ϵ_s and σ are homogeneous functions of Φ and T . The exponents of the scaling laws are therefore expected to be identical with those measured as the droplet concentration is varied.

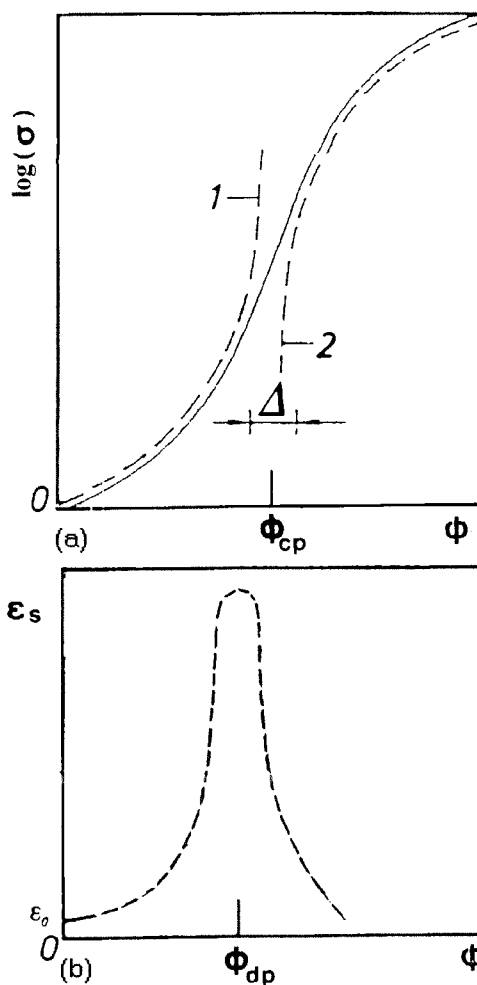


Figure 9.

(a) Theoretical trend of conductivity vs. volume fraction of the conducting phase Φ . Φ_p : percolative concentration. Curves (1) and (2), below and above Φ_p respectively, correspond to the relations $\sigma(\Phi)$ reported in Appendix B. A smooth transition occurs from (1) to (2) in a very narrow concentration interval (Δ) in the neighborhood of the percolative concentration. (b) Theoretical trend of the static permittivity against the volume fraction of the conducting phase. See [14]. Symbols were unified according to Appendix B.

Under the hypothesis that the microemulsion is a binary mixture with a complex permittivity $\epsilon^* = \epsilon_{is} - \sigma_1/\omega\epsilon_0$, where, $i = 1, 2$, $\sigma_2 = 0$ and $|\epsilon_1^*| \gg |\epsilon_2^*|$ then the system undergoes through a percolative transition if the scaling laws reported in Appendix B are verified.

The values of the exponent μ and s , define whether the process is percolative and the type of mechanism involved namely static $\mu \simeq 1.5$ to 2.0, $s \simeq 0.6$ to 0.7, and dynamic $\mu \simeq 1.5$ to 2.0; $s \simeq 1.2$.

For w/o microemulsions a percolative picture for the

transition involves, in any case, the formation of clusters of water globules which are sufficiently close to each other so that an efficient transfer of charge carriers between the globules may occur.

In static percolation, the globules coalesce leading to the formation of a doubly continuous structure in which the system is connected through continuous water channels.

In dynamic percolation, the globules do not lose their identity. Clusters may form in presence of attractive interactions. In w/o microemulsions clusters continuously rearrange themselves because of Brownian motion. Therefore a charge can propagate by either hopping to a neighboring globule, or via the diffusion of the host globule.

A result of percolation transition analysis of the temperature dependence of both the conductivity and the static permittivity of PFPE w/o microemulsions experimental data, performed in terms of scaling laws and evaluation of the scaling exponents, is reported in Figure 10(a) and (b), for two different samples. Our findings strongly support the presence of percolative behavior of the actual system. The values of the exponents calculated support also that a dynamic type of percolative process is involved [19].

Further work on the characterization of the percolation transition of perfluoropolyether water-in-oil microemulsions, as a function of the volume fraction Φ of the dispersed conductive phase, will be published elsewhere.

5. APPENDIX A

A dielectric material contained between the plates of an ideal parallel - plate capacitor can be represented by an equivalent parallel RC electrical circuit having capacitance

$$C = k\epsilon_0\epsilon' \tag{1}$$

and conductance

$$G = \omega k\epsilon_0\epsilon'' + k\sigma \tag{2}$$

where ϵ_0 is the permittivity of free space, $\epsilon' - j\epsilon''$ is the complex permittivity of the medium ($j^2 = -1$), σ is the frequency invariant contribution to the conductivity, ω is the angular frequency ($2\pi f$) and k is the cell constant depending only upon the cell geometry for such ideal case. In our case a stray capacitance C_o has to be added in parallel to the previous circuit and a self - inductance L_s and a resistance R_s have to be added in series [11]. In fig. 3 the electrical equivalent circuit is drawn. At each frequency the latter circuit can be described as an RC parallel, say $R_M C_M$; as the experimentally measured quantities are the impedance magnitude $|Z|$ and the phase angle

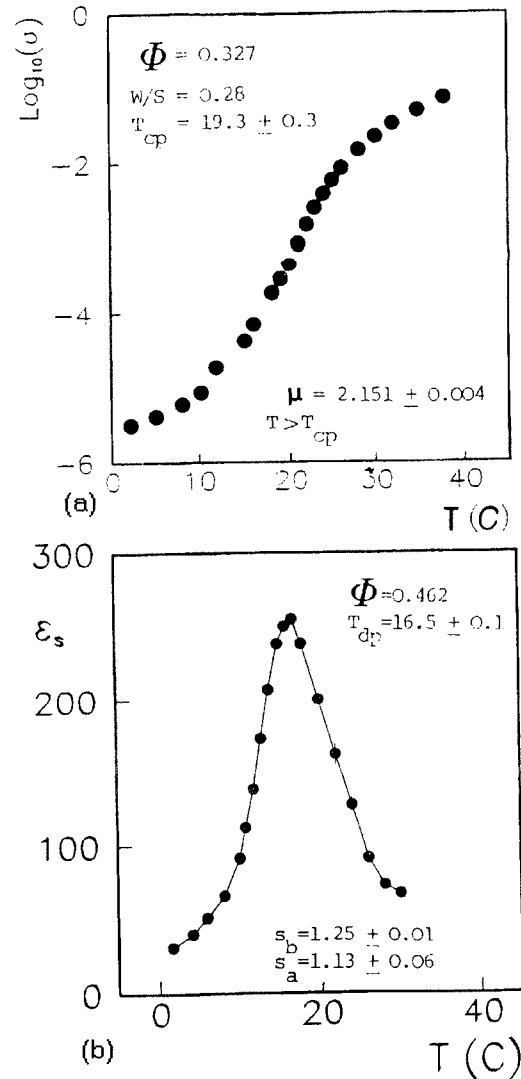


Figure 10.

Percolation analysis. Typical temperature dependence of: (a) the electrical conductivity. Note the change in conductivity of about four orders of magnitude. To be compared with the $\sigma(T)$ behavior reported in Figure 7 for a non-percolative sample, in the same temperature interval. (b) The static permittivity. Dots: experimental points.

φ , then $R_M = |Z|/\cos\varphi$, $C_M = -\sin\varphi/\omega|Z|$. Equating the circuit shown in fig. 3 to the $R_M C_M$ circuit, the sample resistance $R = 1/G$ and the sample capacitance C can be calculated as follows

$$R = \frac{R_M - R_s b}{b} + \frac{\omega^2 (bL_s + \tau_M R_M)^2}{b(R_M - R_s b)} \tag{3}$$

$$C = \frac{bL_s + \tau_M R_M}{(R_M - R_s b)^2 + \omega^2 (bL_s + \tau_M R_M)^2} - C_o \tag{4}$$

where $\tau_M = R_M C_M$ and $b = 1 + \omega^2 \tau_M^2$. The trend of ϵ' and ϵ'' vs. frequency typical of the dielectric absorption due to the interfacial polarization (or Maxwell - Wagner polarization) is

$$\epsilon' - j\epsilon'' = \epsilon_h + \frac{\epsilon_l - \epsilon_h}{1 + (j\omega\tau_s)^\alpha} \quad (5)$$

In the latter equation ϵ_l is the real part of the dielectric permittivity extrapolated at zero frequency (static permittivity of the sample), ϵ_h is the plateau high frequency value of ϵ' , τ_s is the relaxation time and α is the spread parameter.

6. APPENDIX B

For what concerns the scaling laws for percolative processes we recall that in case of a percolation transition characterized by a percolation threshold Φ_p or T_p the static dielectric constant and the conductivity of the microemulsion follow the scaling laws here summarized For $\Phi < \Phi_p$ (before threshold)

$$\epsilon_s = A\epsilon_{2s}(\Phi_{dp} - \Phi)^{-s} \quad (6)$$

$$\sigma = A\sigma_2(\Phi_{cp} - \Phi)^{-s} \quad (7)$$

For $\Phi > \Phi_p$ (after threshold)

$$\epsilon_s = c_1\epsilon_{2s}(\Phi - \Phi_{dp})^{-s} \quad (8)$$

$$\sigma = c_1\sigma_1(\Phi - \Phi_{cp})^\mu \quad (9)$$

For $T < T_p$ (before threshold)

$$\epsilon_s = B\epsilon_{2s}(T_{dp} - T)^{-s} \quad (10)$$

$$\sigma = B\sigma_2(T_{cp} - T)^{-s} \quad (11)$$

For $T > T_p$ (after threshold)

$$\epsilon_s = B_1\epsilon_{2s}(T - T_{dp})^{-s} \quad (12)$$

$$\sigma = B_1\sigma_2(T - T_{cp})^\mu \quad (13)$$

where Φ is the volume fraction of the dispersed phase (water+surfactant/total); the lower-case subscripts d and c stay for dielectric and conductive. The exponents s and μ define whether the process is percolative and the type of mechanism involved. For static percolation $\mu \sim 1.5 - 2.0$ and $s \sim 0.6 - 0.7$; for dynamic percolation $\mu \sim 1.5 - 2.0$ and $s \sim 1.2$.

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