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The static electrical conductivity of water-in-oil microemulsions below percolation threshold

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Abstract

We study the static electric conductivity in water-in-oil microemulsion systems both in the droplet phase and in the vicinity of a percolation transition in the non-percolating region. We discuss the mechanisms of conduction in the two regimes. In particular, we interpret the behavior of conductivity far from percolation in terms of charge fluctuations and close to percolation in terms of collection of relaxation times connected to the presence of a polydisperse set of independent fractal clusters.

1. Introduction

Microemulsions are homogeneous, thermodynamically stable solutions composed of water droplets immersed in an oil bath, where the two immiscible components are separated by a monomolecular layer of amphiphilic molecules. These systems have attracted attention, besides for their practical interest in applications, because of their aggregation patterns which span a wide variety of morphologies and thus make them a very interesting model system to study complex fluids [1,2].

In this paper we analyze in detail the low-frequency conductometric behavior of a particular microemulsion system, i.e. a water-in-oil microemulsion composed of water, decane as a continuous non-conducting phase and AOT (sodium diethyl-

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hexyl-sulfosuccinate) as ionic surfactant, for a fixed molar ratio of water to AOT. This system, denoted hereafter as WAD, represents a very interesting model system for the study of different phenomena occurring in supramolecular liquids, such as cluster aggregation, critical point anomalies [3] and percolative transitions [4]. Two different regimes can be evidenced in the conductometric behavior of this system, in the temperature and composition plane. In the first regime the conduction is governed by the migration of isolated charge carriers (the single water droplets) while in the second one, occurring as the temperature T or the water volume fraction Φ are increased, a collective behavior prevails, due to the formation of clustered aggregates progressively spanning the whole system. It is noteworthy that there is a continuous evolution from a conduction essentially due to Brownian motion of charged water droplets to that dominated by motion of charges within connected clusters of water channels over large scale length. Close to percolation, the conductive process is mainly due to the hopping of charges from one droplet to another. This process, known as dynamical percolation [5], drives the system from a collection of isolated non-interacting droplets to a connected system whose bicontinuous structure allows conduction in water channels.

We will briefly mention some of the results recently obtained on WAD microemulsions over a wide range of temperature and composition and will summarize the theoretical framework that allow a very satisfactory understanding of the conductivity phenomena. In particular, we focus here on some aspects concerning the static electrical conductivity based on a new phenomenological model of conduction we proposed [6], related to clustering of the microemulsion droplets and migration of charges within the aggregates. Owing to the different regimes of conduction occurring in microemulsions, well below the percolation and close to it, we will discuss separately the conductivity behavior of dilute systems, in absence of percolation, and that at higher concentration, when percolation is the relevant phenomenon.

2. The electrical conductivity well below the percolation threshold

In this region, the system is composed of a collection of non-interacting water droplets coated by a monomolecular layer of surfactant, uniformly dispersed in a continuous non-conducting oil phase. The effective electrical conductivity σ of this homogeneous dispersion is a statistical property which depends on the conductivity of the two constituents (continuous phase σ_A and dispersed phase σ_B) and on their geometrical structures and shapes. From a general point of view, the conductivity σ can be expanded in a series of the form

$$\sigma = \sigma_A(1 + K_1\Phi + K_2\Phi^2 + \dots). \quad (1)$$

If the conduction mechanism is confined to the interfacial polarization related to the bulk electrical properties of the constituents only, the first term in the above expansion,

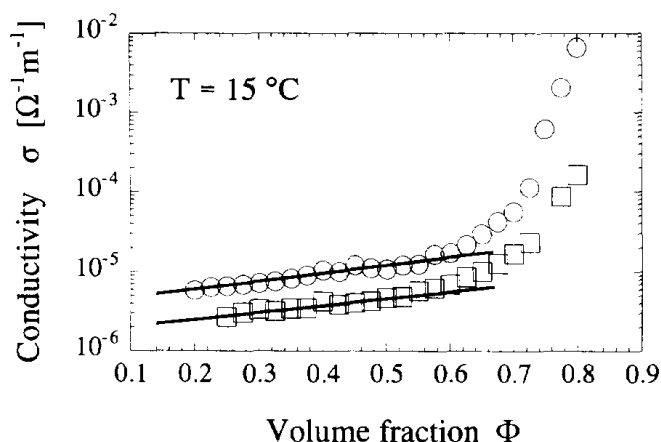


Fig. 1. The static electrical conductivity σ as a function of fractional volume Φ at the temperature of 15 °C. (○) in presence of added salt (10^{-2} M NaCl); (□) in absence of added salt. The straight lines are the calculated values according to the Eicke–Hall theory [Eq. (3)], with an hydrodynamic radius R of 80 Å (in absence of added salt) and 60 Å (in presence of added salt). The deviation from a straight line as the fractional volume Φ is increased indicates the onset of percolation.

in the mean field approximation [7], is linked to the reduced polarizability through the relation

$$K_1 = 3 \frac{\sigma_B - \sigma_A}{\sigma_B + 2\sigma_A}. \quad (2)$$

In the case of water-in-oil microemulsion, Eqs. (1) and (2) are unable to account for the observed behavior of the static conductivity, both as a function of temperature and as a function of composition. Any improvement requires additional information on the morphology of the system dealing with the particular conduction mechanism involved. A particular mechanism based on charge fluctuation has been proposed by Eicke [8] and more recently by Hall [9]. The effectiveness of such mechanism has been verified very carefully in the systems we have studied [10, 11]. The conductivity behavior as a function of temperature T , or equivalently on composition Φ , reflects the ionization of the surfactant molecules giving rise to a charge fluctuation mechanism which makes each water droplet charged, thus contributing, by means of Brownian movement, to the overall conductivity. Within this theory, the conductivity σ is given by

$$\sigma = \Phi \frac{e^2 \sum_{-\infty}^{+\infty} z^2 \exp(-z^2 e^2 / 2\epsilon R k_B T)}{8\pi^2 R^4 \eta \sum_{-\infty}^{+\infty} \exp(-z^2 e^2 / 2\epsilon R k_B T)}, \quad (3)$$

where ϵ and η are the dielectric constant and viscosity of the oil phase (decane, in our case), respectively, ze the electric charge of each water droplet, $k_B T$ the thermal energy and R_1 the hydrodynamic radius of the dispersed particles. Since the anionic head groups and counterions are considered to reside inside the interface of the surfactant coat with the aqueous core, to make a charged droplet it is only necessary for the droplet to exchange surfactants without counterions. Some typical results are shown in Fig. 1, where the conductivity σ is plotted as a function of the fractional volume

Φ for two different WAD microemulsions, i.e., a three-component system and a four-component microemulsion, the aqueous phase of which has been modified by adding a small amount of a simple salt (10^{-2} M NaCl). As can be seen, a very good agreement is obtained for low Φ values, below percolation. When the droplet concentration increases, the system undergoes a percolative transition and a different transport mechanism occurs.

3. The electrical conductivity close to the percolation threshold

When connectivity between the conducting droplets is achieved due to the clustering process, driven by the interdroplet potential, either by transient merging of different droplets or by formation of stable water channels, a very pronounced increase of conductivity is observed. Such increase has been analyzed in the frame of percolation theory. According to the dynamic percolation model [5], the increase in conductivity is due to a cooperative process dominated by the motion of charged carriers on fractal clusters, whose average size diverges at percolation. In this conducting regime, when approaching the threshold in temperature at constant composition, the static conductivity σ is characterized by power laws defined by percolative indices, according to

$$\sigma_0 \approx |T - T_p|^{-s}, \quad T < T_p, \quad (4)$$

$$\sigma_0 \approx |T - T_p|^\mu, \quad T > T_p, \quad (5)$$

below and above the percolation temperature T_p , respectively. Similar power laws are valid when approaching the percolation line in composition at constant temperature. The diverging behaviors are valid close to the percolation line, but not in a narrow region around it, where the conductivity reaches a finite value. A typical plot of $\ln \sigma$ vs. $\ln |T - T_p|$ in the vicinity of the percolation threshold for WAD microemulsions at different volume fraction Φ is shown in Fig. 2. The power law behaviors of the static and dynamic percolation with exponent $\mu = 1.80$ and $s = 1.16$, respectively, are also shown. As can be seen, although straight lines of appropriate slopes are observed above and below percolation, deviations from a power law occur very close to it. We have recently proposed a new approach [6, 12] which gives a more detailed description of the dynamic percolation, including both the power law behavior on approaching the threshold and the saturation in the static conductivity very close to it. In order to derive an expression describing the frequency dependence of the complex conductivity of a microemulsion, we start, within the framework of the effective medium approximation for heterogeneous systems, considering the conductivity of a cluster containing k droplets, each of them characterized by a complex conductivity $\tilde{\sigma}_B = \sigma_B + i\omega\epsilon_B$ and dispersed in a matrix of complex conductivity $\tilde{\sigma}_A = \sigma_A + i\omega\epsilon_A$. The formation of large aggregates, characterized by a fractal

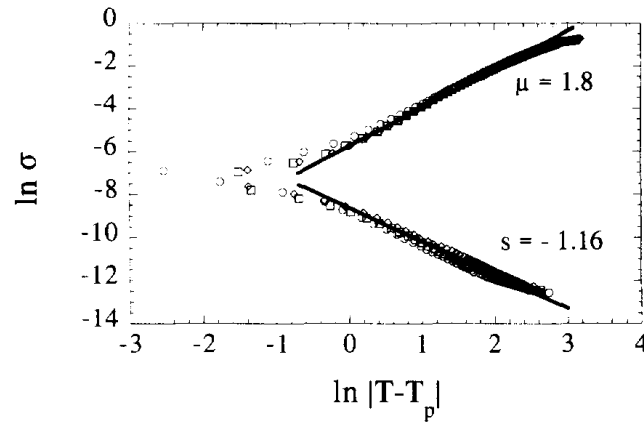


Fig. 2. A typical plot of $\ln \sigma$ vs $\ln |T - T_p|$ for microemulsions at different volume fraction Φ in presence of added salt (10^{-2} M NaCl). (\square) $\Phi = 0.425$, (\circ) $\Phi = 0.525$, (\diamond) $\Phi = 0.575$. The two straight lines represent the power laws above and below percolation with exponents $\mu = 1.80$ (static percolation) and $s = -1.16$ (dynamic percolation). Deviations from a power law behavior very close to percolation are also evident.

dimension D , allows the charge carriers to perform anomalous diffusion on the fractal cluster, originating a dipole moment fluctuation or, in the frequency domain, a conductivity dispersion which occurs for typical microemulsion systems in MHz region. In term of cluster relaxation processes, the complex conductivity $\tilde{\sigma}(\omega)$ can be written as

$$\tilde{\sigma}(\omega) = \int_1^{\infty} dk \ c(k) \left(\sigma_{k0} + i\omega \varepsilon_{k\infty} + i\omega \frac{\Delta_k}{1 + i\omega \tau_k} \right), \quad (6)$$

where σ_{k0} is the low-frequency limit of the k cluster conductivity, $\varepsilon_{k\infty}$ is the high-frequency limit of permittivity. Δ_k and τ_k are the dielectric increment and the relaxation time of the k cluster. $c(k)$ takes into account the cluster size distribution. Once a typical scaling expression for $c(k)$ is considered, characterized by a power law behavior with index τ and cutoff k_c [13], taking into account the fractal and dynamical properties of each cluster, Eq. (4) can be analytically calculated close to T_p as shown in Refs. [6, 12].

The complex conductivity we derived depends on five parameters, σ_A , σ_B , ε_A and ε_B , the four materials parameters of the two-component system and k_c . The parameter k_c is a physical quantity extracted from the experimental data by the fitting procedure to the frequency dependence of conductivity and permittivity. Note that any theory would need essentially the same number of parameters, which are the minimal set to describe the relaxation. Even the use of a simple interpolation formula like Cole–Davidson's needs five parameters, namely the zero-frequency conductivity and the high-frequency permittivity, the relaxation amplitude and time and the characteristic Cole–Davidson exponent. Moreover, these quantities would have a dependence from the distance from percolation, which is obtained in our case by means of k_c . k_c is related to the dimensionless distance from the threshold $|T - T_p|/T_p$

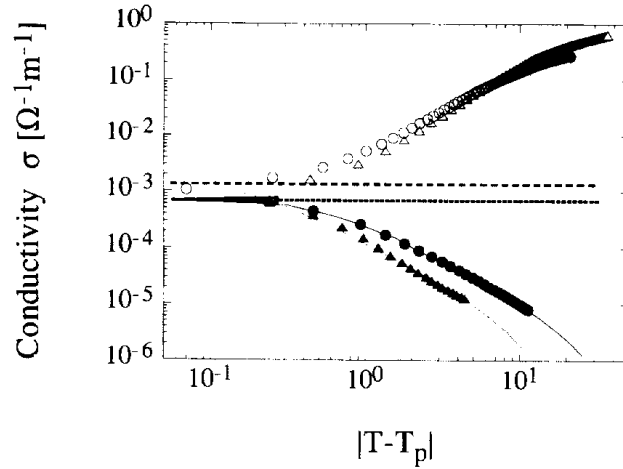


Fig. 3. The two branches of electrical permittivity above (open symbols) and below (full symbols) percolation for WAD system at water to surfactant molar ratio $X = 40.8$ as a function of $(T - T_p)$ (circles: $\Phi = 0.575$, in presence of added salt, 10^{-2} M NaCl) (triangles: $\Phi = 0.400$). The full lines, below percolation, represent the calculated values according to Eq. (6), giving the observed conductivity behavior up to the percolation threshold. The horizontal lines indicate the finite value of the conductivity at percolation.

by the relation

$$k_c = \left(\frac{\xi_0}{R_1} \right)^D \frac{|T - T_p|^{-\nu D}}{T_p}, \quad (7)$$

where ξ_0 is the amplitude of the percolation correlation length ξ divergence and ν is the index of it

$$\xi = \xi_0 \frac{|T - T_p|^{-\nu}}{T_p}. \quad (8)$$

It is easy to show from Eqs. (6) and (8) that in a region not too close to the threshold the static conductivity σ behaves as

$$\sigma \approx \frac{|T - T_p|^{-\nu(D-1)}}{T_p} \approx |T - T_p|^{-s}, \quad (9)$$

where $s = \nu(D - 1)$ is the index of the divergence of the static conductivity.

Fig. 3 shows the measured static conductivity as a function of temperature for a WAD system at two different volume fractions, in presence and in absence of added salt. As can be seen, at the percolation temperature T_p , the static conductivity σ reaches a finite value, related to the small but finite conductivity of the oil phase. The power law $\sigma \approx |T - T_p|^s$ can be observed only in a finite window not too close to T_p . On the contrary, Eq. (6) gives a detailed description over the whole branch of conductivity below percolation, yielding exactly the value of σ at $T = T_p$.

The above model, giving quantitative expressions for both conductivity and permittivity in the entire frequency range of the percolative relaxation phenomenon, has been applied in different microemulsion systems of different composition, in different temperature and frequency ranges, with a very good agreement in all cases [12].

References

- [1] S.H. Chen, J.S. Huang and P. Tartaglia, eds., *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solution*, NATO ASI Series, Vol. 369 (1991).
- [2] S. Safran and N.A. Clark, eds., *Physics of Complex Supramolecular Fluids* (Wiley, New York, 1987).
- [3] J. Rouch, P. Tartaglia and S.H. Chen, *Phys. Rev. Lett.* 71 (1993) 1947.
- [4] C. Cametti, P. Codastefano, P. Tartaglia, J. Rouch and S.H. Chen, *Phys. Rev. Lett.* 64 (1990) 1461.
- [5] G.S. Grest, I. Webman, S. Safran and A.R.L. Bug, *Phys. Rev. A* 33 (1986) 2842.
- [6] C. Cametti, F. Sciortino, P. Tartaglia, J. Rouch and S.H. Chen, *Phys. Rev. Lett.* 75 (1995) 569.
- [7] T. Hanai, in: *Emulsion Science*, ed. P. Sherman (Academic Press, New York, 1968).
- [8] H.F. Eicke, M. Borkovec and B. Das-Gupta, *J. Phys. Chem.* 93 (1986) 314.
- [9] D.A. Hall, *J. Phys. Chem.* 94 (1990) 429.
- [10] A. Di Biasio, C. Cametti, P. Codastefano, P. Tartaglia, J. Rouch and S.H. Chen, *Phys. Rev. E* 47 (1993) 4258.
- [11] C. Cametti, P. Codastefano, P. Tartaglia, S.H. Chen and J. Rouch, *Phys. Rev. A* 45 (1992) R5358.
- [12] F. Bordi, C. Cametti, J. Rouch, F. Sciortino and P. Tartaglia, *J. Phys. Conds. Matter*, submitted.
- [13] D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor and Francis, London, 1992).