FLORE
Repository istituzionale dell'Università degli Studi di Firenze

Percolation in fluorinated microemulsions: A dielectric study

(Article begins on next page)

27 September 2024

M.G. Giri
M. Carlà
C.M.C. Gambi
D. Senatra
A. Chittofrati
A. Sanguineti

Percolation in fluorinated microemulsions: A dielectric study

M.G. Giri · M. Carlà
C.M.C. Gambi (✉) · D. Senatra
Department of Physics
University of Florence
L.E. Fermi 2
50125 Firenze, Italy

A. Chittofrati · A. Sanguineti
Ausimont
R & D Centre
Colloid Laboratory
Via San Pietro 50
20021 Bollate, Milan, Italy

Abstract This work deals with the dielectric investigation of fluorinated water-in-oil microemulsions with perfluoropolyether (PFPE) compounds. The microemulsion ohmic conductivity and dielectric constant at different temperatures and frequencies have been studied at water to surfactant molar ratio W/S = 11 for monophasic samples having volume fractions of the dispersed phase, ϕ, in the range 0.2 to 0.6. The study as a function of temperature in the interval $-10°$ to $40\,°C$ showed a percolation phenomenon (Phys Rev E (1994) 50:1313). The analysis in terms of scaling laws and the calculation of the scaling exponents indicated that the percolation process is mainly dynamic. Preliminary results are here presented of the study as a function of frequency.

Key words Microemulsion – fluorinated compound – percolation – dielectric study – frequency dependence

Introduction

Since the pioneering work of ref. [1] the percolation phenomenon has been demonstrated to take place in water-in-oil microemulsions with hydrogenated oil for both water-based [1–9] and waterless microemulsions [10–12], and for both ionic [1–13] and non-ionic surfactants [13] (in this last case an electrolyte is added to the system). Recently, the percolation phenomenon has also been found in fluorinated microemulsions [14] composed of perfluoropolyether compounds, of which both the surfactant tail and the oil are perfluorinated.

When microemulsions are composed of aggregates of more or less spherical shape in Brownian motion in a continuous medium and sufficiently close to each other so that an efficient transfer of charge carriers between aggregates can take place, the percolation transition corresponds to the appearance of a cluster of infinite size. In practice, for a sample of finite size the increase of the number density of dispersed aggregates in the continuous medium forms one cluster which connects the system from one side to the opposite side (for example, the two electrodes of a dielectric cell containing the sample) at the percolation threshold. We recall that for hard-spheres dispersed randomly in an insulating continuous medium, the percolation threshold corresponds to the close-packing limit which is 0.65 expressed as volume fraction of the dispersed conducting phase. Microemulsions composed of dispersed aggregates in a continuous medium are systems of interacting objects. Therefore the interaction between the aggregates does play an important role [15, 16] in the correlation of positions leading to percolation thresholds at volume fractions lower than 0.65. Moreover, the aggregates give rise to a cluster of infinite size, or percolate, either for an increase of the number density of the aggregates themselves [2–6, 10, 11], or for a temperature increase [3, 7, 8, 14], or a pressure increase [12], etc. The actual description of the percolation phenomenon corresponds to what is called dynamic percolation [15, 16]; it differs from static

percolation. The latter implies a coalescence of droplets, as the percolation threshold is approached, leading to the formation of one continuous channel of the dispersed medium (bicontinuous structure [15, 16, 9, 17]).

In ref. [14] we reported about the behavior of the static dielectric constant and the conductivity versus temperature of a fluorinated water-in-oil microemulsion at constant water to surfactant molar ratio W/S = 11 for which previous light scattering investigations at $T = 25\,°C$ [18] demonstrated that water droplets of hydrodynamic radius $30\,\text{Å}$ interact via an attractive potential (second virial coefficient $\alpha = -8$). Analysis in terms of scaling laws and the calculation of the scaling exponents indicate a dynamic percolation process with an exponent $s \simeq 1.2$ below the thermal threshold for all the samples studied and above the thermal threshold for intermediate ϕ values $0.33 < \phi < 0.48$, where ϕ is the volume fraction of the dispersed phase (water + surfactant)/(water + surfactant + oil). The exponents of static percolation $s \simeq 0.7$ were found above the threshold at $\phi < 0.33$ and $\phi > 0.48$. For all the samples μ exponents $\simeq 2$ were found as expected for both static and dynamic percolation.

In this paper the percolation phenomenon exhibited by the system at W/S = 11 is analyzed by measuring the dielectric constant as a function of frequency.

Materials

Water was taken from a Millipore Milli-Q system. The oil and the surfactant are PFPE compounds of general formula reported in ref. [14]. The surfactant molecular weight is 710, with a molecular weight distribution of 95% by gaschromatographic analysis. The surfactant polar head is a $-COO^-NH_4^+$ group. The oil molecular weight is 900, the density $1.8\,\text{g/cm}^3$ and the viscosity $6.2\,\text{cp}$. The ternary system water, fluorinated oil and fluorinated surfactant systematically studied in the range 10° to 80°C shows a monophasic domain throughout this range: the extension of the monophasic region changes as a function of temperature. The phase diagram behavior in the range 20° to 50°C as well as the binary phase diagrams related to the system under investigation are reported in [19]. The experimental procedure used to study the dielectric behavior of the PFPE microemulsions is described in ref. [20].

Results and discussion

From the point of view of the dielectric properties, one microemulsion sample can be considered a conductor-insulator mixture, where the conductive part is the aque-
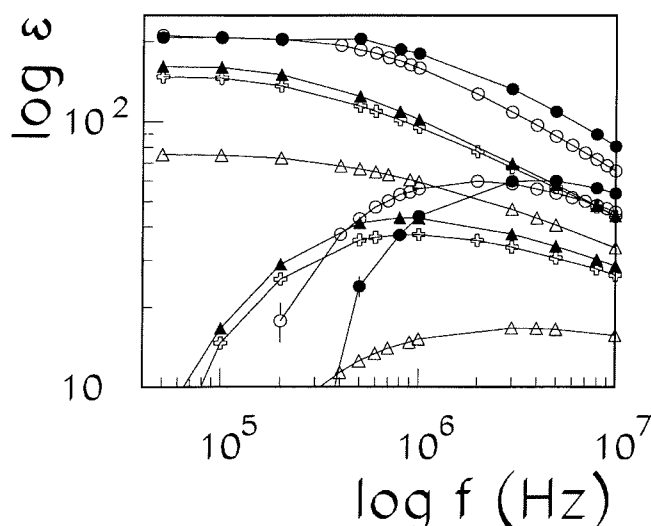

Fig. 1 The ε' and ε'' frequency dependence at constant temperature $T = 20\,°C$ for samples with $\phi = 0.501$ (full circles), $\phi = 0.462$ (open circles), $\phi = 0.395$ (full triangles), $\phi = 0.361$ (open plus) and $\phi = 0.327$ (open triangles). The logarithmic scales are decimal for all the figures

ous region and the insulating part the oily one. Thus the microemulsion complex permittivity ε^* at constant temperature and pressure, is a function of the complex permittivities of the dispersed phase (water) ε_1^*, of the continuous phase (oil) ε_2^*, of the ϕ value, of the geometry of the system and of the interactions taking place within the system. The models based on mean-field theories that yield good results when interactions are weak, i.e., for low ϕ values, and when the microemulsion can be considered as macroscopically homogeneous, no longer apply when the dispersed particles cannot be considered isolated, i.e., when clusters of varying sizes form. In this case the concept of percolation can successfully be used.

In this paper we present the experimental frequency dependence of the complex permittivity for samples close to and at the percolation threshold. In Fig. 1 the real (ε') and the imaginary (ε'') parts of the complex permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) are reported as a function of frequency at $T = 20\,°C$ for samples with different ϕ values. In Fig. 2 the same parameters are reported as a function of frequency for one sample with $\phi = 0.327$ at different temperatures in the range 2° to 26°C. We point out that the study as a function of ϕ performed at $T = 20\,°C$ gives a percolation threshold $\phi_p = 0.401$ [21].

The frequency dependence of the complex permittivity for a conductor-insulating mixture in the frame of the percolation theory takes the form [3, 22]:

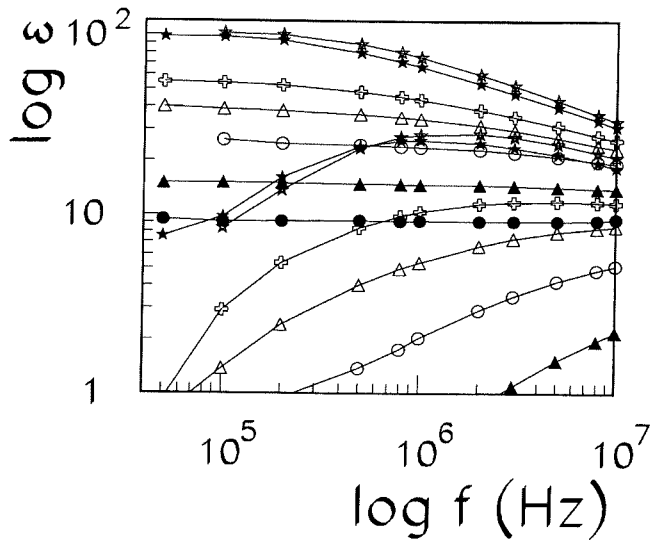$$\varepsilon^*(\omega) = E \cdot \exp[\,j\pi(1 - u)/2\,] \cdot \omega^{u-1}, \tag{1}$$

Fig. 2 The ε' and ε'' frequency dependence for the sample with $\phi = 0.327$ at different temperatures: 2 °C (full circles), 8 °C (full triangles), 12 °C (open circles), 16 °C (open triangles), 18 °C (open plus), 22 °C (full stars), 24 °C (open stars). The ε'' (ω) curve at $T = 2$ °C is lower than the scale of the picture

where E is a real value and u is a critical exponent. Equation (1) implies that both $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ exhibit a ω^{u-1} frequency dependence and that the loss angle Δ defined by $\tan \Delta(\omega) = \varepsilon''(\omega)/\varepsilon'(\omega)$ is independent of frequency and equal to $\pi(1 - u)/2$. We recall that, for such a conductor-insulator mixture, the conductivity as well as the static dielectric constant scaling laws as a function of $|\phi - \phi_p|$ are characterized by two critical exponents μ and s whose value is $\mu \simeq 2$ for both static and dynamic percolation, while is $s \simeq 0.7$ for static and $\simeq 1.2$ for dynamic percolation. The exponent u is related to μ and s by the equation $u = \mu/(\mu + s)$. This implies a value of about 0.625 for dynamic percolation and of about 0.741 for static percolation. These two u values give loss angle tangent of 0.668 and 0.431 for dynamic and static percolation, respectively.

The ε' and ε'' curves of Fig. 1 have a similar trend for the different ϕ values. In the frequency range investigated, the analysis in terms of scaling laws can be performed only for the $\varepsilon'(\omega)$ functions. Increasing the ϕ value, a linear dependence in logarithmic scale is found at $\phi = 0.462$ according to Eq. (1); from the slope of the straight line, reported in Fig. 3, the u exponent is deduced to be 0.59, a value indicating a dynamic percolation regime. The ε' and ε'' curves of Fig. 2 have a similar trend at the different temperatures and, as for the curves of Fig. 1, in the frequency range investigated only the $\varepsilon'(\omega)$ curves can be analyzed in terms of scaling laws. Increasing the temperature, a linear frequency dependence in logarithmic scale is found at $T = 24$ °C; from the slope of the straight line (see

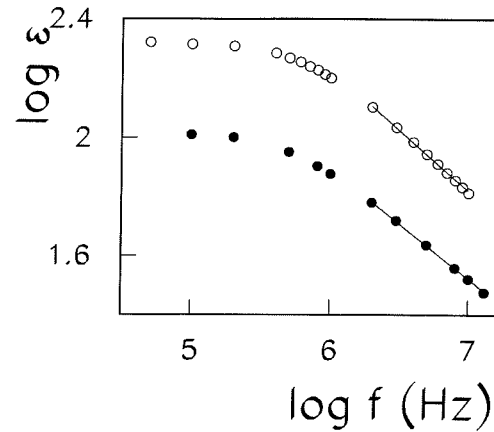**Fig. 3** Experimental frequency dependence of ε' and straight line for the calculation of the critical exponent u. The error bars are standard deviations. Sample with $\phi = 0.462$ at $T = 20$ °C (open circles). Sample with $\phi = 0.327$ at $T = 24$ °C (full circles)
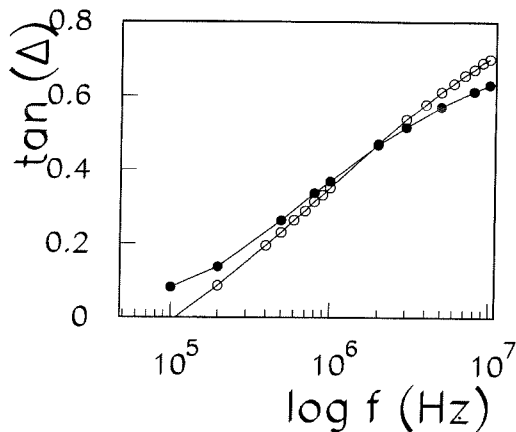

Fig. 4 The tangent of the loss angle as a function of frequency for the samples of Fig. 3 with identical symbol meaning

Fig. 3) a u exponent equal to 0.628 is deduced, a value which indicates a dynamic percolation regime. In Fig. 4 the tangent of the loss angles increases in both cases as a function of frequency up to values higher than 0.6. The u exponents and the $\tan \Delta$ values support the interpretation that a dynamic percolation process occurs in the microemulsions studied.

By comparing the latter results with those of ref. [14] the following conclusion can be drawn. For the sample with $\phi = 0.462$, we found a thermal threshold of 16.5 °C (from permittivity) and of 12.5 °C (from conductivity) with exponents typical of dynamic percolation below and above the thermal thresholds. As the curve of Fig. 3 is at 20 °C the sample is above threshold; furthermore as $\phi_p = 0.401$ the sample is above threshold also from the

point of view of concentration. For the sample with $\phi = 0.327$ for which the thermal threshold is 22.8 °C (from permittivity) and 19.3 °C (from conductivity), we found a dynamic percolation process below and a static percolation process above the thermal threshold. However, the results of this paper at $T = 24$ °C (see Figs. 3 and 4), i.e., above the thermal threshold, indicate a dynamic percolation process. Further work is required.

In conclusion, the study reported here confirms that the percolation phenomenon taking place in fluorinated microemulsion with perfluoropolyethers is of dynamic type.

References

1. Lagues M, Ober R, Taupin C (1978) J Phys Lett (Paris) 39:487–491
2. Van Dijk MA (1985) Phys Rev Lett 55:1003–1005
3. Van Dijk MA, Casteleijn G, Joosten JGH, Levine YK (1986) J Chem Phys 85:626–631
4. Peyrelasse J, Moha-Ouchane M, Boned C (1988) Phys Rev A 38:904–917
5. Peyrelasse J, Boned C (1990) Phys Rev A 41:938–953
6. Cametti C, Codastefano P, Di Biasio A, Tartaglia P (1989) Phys Rev A 40: 1962–1966
7. Cametti C, Codastefano P, Tartaglia P, Rouch J, Chen S-H (1990) Phys Rev Lett 64:1461–1464
8. Cametti C, Codastefano P, Tartaglia P, Chen S-H, Rouch J (1992) Phys Rev A 45:R5358–R5361
9. Knackstedt MA, Ninham BW (1994) Phys Rev E 50:2839–2843
10. Mathew C, Saidi Z, Peyrelasse J, Boned C (1991) Phys Rev A 43:873–882
11. Boned C, Peyrelasse J, Saidi Z (1993) Phys Rev E 47:468–478
12. Boned C, Saidi Z, Xans P, Peyrelasse J (1994) 49:5295–5302
13. Eicke H-F, Meier W, Hammerich H (1994) Langmuir 10:2223–2227
14. Giri MG, Carlà M, Gambi CMC, Senatra D, Chittofrati A, Sanguineti A (1994) Phys Rev E 50:1313–1316
15. Safran SA, Webman I, Grest GS (1985) Phys Rev A 32:506–511
16. Grest GS, Webman I, Safran SA, Bug ALR (1985) Phys Rev A 33:2842–2845
17. Di Biasio A, Cametti C, Codastefano P, Tartaglia P, Rouch J, Chen S-H (1993) Phys Rev E 47:4258–4264
18. Sanguineti A, Chittofrati A, Lenti D, Visca M (1993) J Colloid Int Sci 155: 402–408
19. Chittofrati A, Lenti D, Sanguineti A, Visca M, Gambi CMC, Senatra D, Zhou Z (1989) Progr Colloid Polymer Sci 79:218–225
20. Giri MG, Carlà M, Gambi CMC, Senatra D, Chittofrati A, Sanguineti A (1993) Meas Sci Technol 5:627–631
21. Giri MG, Carlà M, Gambi CMC, Senatra D, Chittofrati A, Sanguineti A (work in progress)
22. Luck JM (1985) J Phys A 18:2061–2078