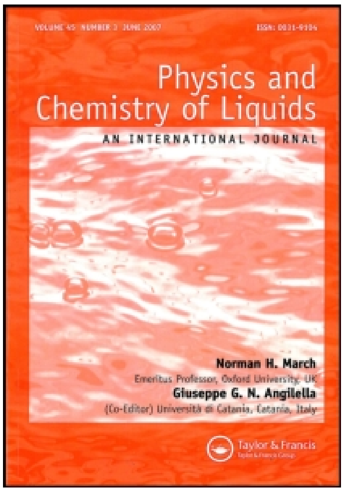

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DIELECTRIC STUDIES ON MICROEMULSIONS-BASED GELS

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Static permittivity and dielectric relaxation measurements in microemulsions-based gels (organogels) were performed. Dielectric spectra have been obtained with a time domain spectrometer in the range 100 KHz to 1 GHz. These systems were composed of AOT/water/iso-octane and gelatin and microemulsions were prepared by changing $W_0 = [\text{AOT/water}]$ and the AOT molarity (M). Experimental results of dielectric parameters as a function of gelatin concentration are presented. It must be pointed out that unlike other techniques no clear percolative behaviour can be deduced from this kind of experimental technique. Assuming an interfacial polarization mechanism, we were able to calculate the basic electrical length regarding the polarization. These results have been analysed by comparing them with those which have been obtained with other experimental techniques.

Keywords: Organogels; polarization; dielectric spectra

INTRODUCTION

As is well-known, microemulsions are disperse systems where it becomes possible to mix water and oil by means of a surfactant [1]. They are able to form manometric liquid structures. On the other hand, gelatin is easily soluble in water but generally it is not so easy to solubilize it in an oil. It must be pointed out that by adding gelatin to reversed microemulsions (W/o) the collagen solubilization in different

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*Corresponding author.

oils [2–4] was possible. This kind of systems is called microemulsion-based-gels (organogels). These compounds present interesting characteristics either from a basic physicochemical point of view or from a technological one. (*i.e.*, in non-linear optic processes, chemical microreactors) *etc.* [5]. In the last years, while they have been actively investigated some of their principal properties like its molecular microstructure still remain an open question. The goal of this work is the study of their dielectric properties like the permittivity and dielectric relaxation process as function of the frequency and the gelatin concentration. The study of these physical magnitudes allow us to make an adequate structure modelization, in order to compare them with those predicted by other experimental techniques.

EXPERIMENTAL

Sample Preparation

The microemulsions were composed of sodium *bis* (2-ethylhexyl) sulfosuccinate (AOT) water and isooctane and gelatin (Fluka). We used the same batch of gelatin without further purification. The gelatin was introduced in powder form to the micellar solution. The system was placed in a thermostatic bath at 50°C. The solution was then stirred for 10–15 minutes. After this time the samples became homogeneous and translucent. Afterwards, the samples were cooled at room temperature (25°C) under continuous stirring. Finally they became optically clear and were stabilized after a week. Their different 'basic' (null gelatin concentration) was prepared by changing the ratio [water]/[surfactant], $W_0 = 30$ and AOT molarity, $M = 0.15$. The ranging gelatin concentration varied from zero up to the gel formation zone which depends on the W_0 and M values. In order to prevent bacterial degradation a very tiny (1 ppm) amount of sodium azide was added to all samples.

Dielectric Measurements

Dielectric measurements were done in the time domain using TDS2 dielectric spectrometer (Dipole TDS, Jerusalem) and low frequency response checked with a Hewlett-Packard HP 4192 A impedance bridge in the frequency domain. The frequency domain technique is well known and consists of the measurement of the capacity and resistance of a calibrated measurement cell filled with the dielectric. From R and C values the complex permittivity is obtained.

Details on the time domain spectroscopic method and set-up are basically the ones described by Feldman *et al.* [6]. Briefly, the method consists of a step pulse that travels along a coaxial line in which the sample holder acts as a line termination. The time domain response function of the system is related to the complex permittivity *via* the Fourier–Laplace transform. The whole procedure of measurement and data treatment in the TDS experiment is carried out automatically. The control process is done in a dialog box between the user and the system. A non-uniform sampling scheme is used. Circulating fluid with a Lauda thermostat, accurate to ± 0.2°C, controlled the temperature of sample.

RESULTS AND DISCUSSION

We have measured the dielectric properties of samples $W_0 = 30$ and $M = 0.15$. Experimental values of this system are shown in Figures 1 to 3 and used for discussion.

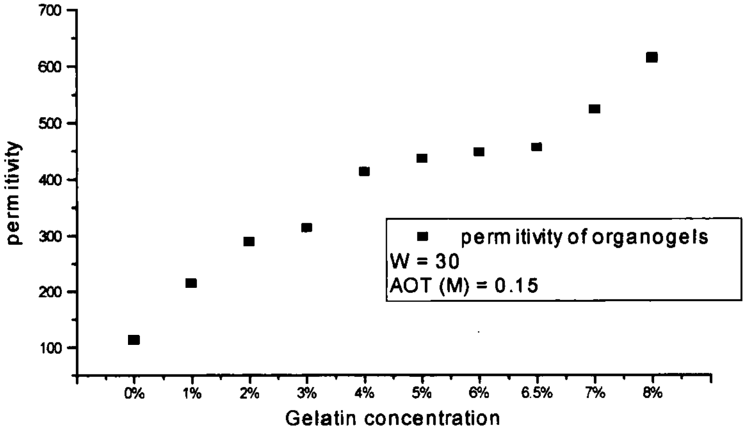

FIGURE 1 Static permittivity of the organogel as a function of the gelatin concentration. ($W_0 = 30$; $M = 0.15$).

Figure 1 shows the static permittivity of a series of microemulsionsbased gels at different concentrations of gelatin. The figure shows a steady increase of the static permittivity with a slight discontinuity at around 5% gelatin. The large values of permittivity suggest that an interfacial mechanism is involved. Figure 2 shows the static permittivity of aqueous solutions of gelatin covering the same concentration range as the microemulsion series. We can see the same qualitative behavior, although the permittivity values are even larger. Figure 3 shows the relaxation frequency corresponding to the same samples of Figure 1. We can distinguish two regions, below and above 5% gelatin, for which the relaxation time remains constant.

Other experimental techniques (conductivity [4], viscosity and electric birefringence [7]) also show a sharp transition between 5% and 9%, depending on W_0 and M values. Our dielectric data suggest also a transition in that range, although none of the data (static permittivity and relaxation time) exhibits a large growing of properties after the transition, suggesting a percolation effect.

Different models for the structure of these microemulsions have been proposed. One of them [2, 3, 8] assume that the water droplets surrounded by surfactant are connected by gelatin molecules that are also partially inside the droplets. An alternative model [9] considers that a gelatin–water network is covered by the surfactant and coexists

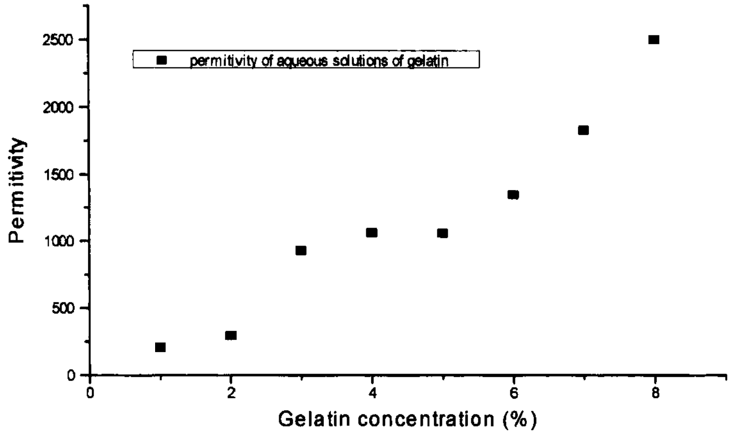

FIGURE 2 Static permittivity of the aqueous solution of gelatin as a function of the gelatin concentration.

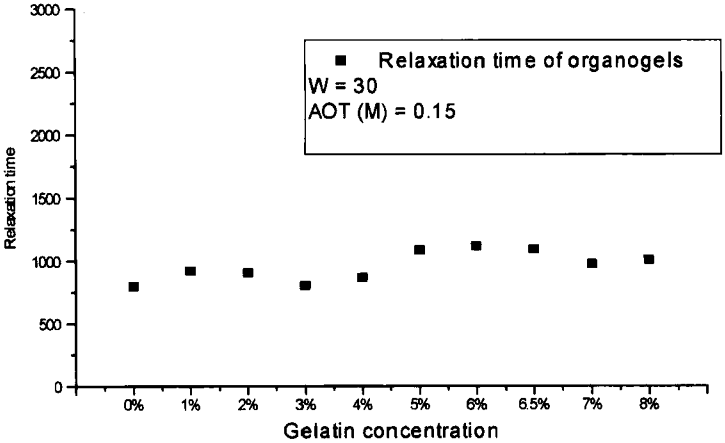

FIGURE 3 Relaxation time of the organogel as a function of the gelatin concentration ($W_0 = 30$; $M = 0.15$).

with the microemulsion nanodroplets. These models are at present under controversy.

From our experimental data, we can see that the trend on the permittivity is similar for the water–gelatin solutions and for the organogel, giving the bases to consider that the gelatin network is responsible for the dielectric behavior of the latter. This, plus the huge values of the permittivity when the gelatin content is increased, are the rationale to interpret the data as an interfacial effect [10]. Ions moving along gelatin network produce an induced polarization that is much larger than any molecular mechanism of polarization. For lower concentration the gelatin–water droplets covered by the surfactant will produce a limited path for the movement of ions. When the concentration increases, gelatin molecules are linking the nanodroplets up to a transition to the state in which large clusters are formed. At this stage the size of the path along which ions can move is larger increasing the permittivity, which is shown by the transition. After that, the 'gelatin bridges' are steadily increasing in size with the consequent slow increase in the permittivity.

There are two aspects that we must be considered under this model for interpretation. The first one is why the viscosity [4, 7] increases abruptly with gelatin concentration, while the permittivity does not. Linkage between droplets may bot be isolated "dumbbells" but a real network does. This network will increase the viscosity while the permittivity value depends on the path length for the ions in the direction of the electric field.

The second aspect to be considered is the behavior of the relaxation time. It remains constant at each side of the transition, which is telling us of a limited path for the ions. This looks as a contradiction to the previous assessment on the behavior of static permittivity. Either the increasing of permittivity is due to an increasing *number* of entities of the same effective length, consequently of the same relaxation time, or, alternatively, that the network has nodes (the droplets) that 'isolate' one section from the other. In both cases we will have the same behavior. The first alternative is in contradiction to the results of electric birefringence [7] that show an increase of the mechanical structural relaxation time, indicating an increase in the physical length, rather that an increase in the number of entities. However, the electrical length regarding the polarization, is kept at the same size.

It is worth recalling that the interfacial polarization – due to the ions moving on the surface – depends on the surface conductivity and not on the bulk conductivity, that may follow a different behavior.

We can estimate the path length using the expressions given by Shwartz [11] for simple colloidal systems.

Within such a theory the length will be

$$l = \sqrt{2uk_{\mathrm{B}}T} \tag{1}$$

where u is the mobility of ions, k_{B} the Boltzmann constant, and T the absolute temperature. The estimation of ion mobility is difficult since in the formula (1) it means surface mobility. This mobility may differ from the bulk mobility. However, we can make an estimation by using for Na^+ a value of 3.1 × 10 11 m, s-1 N-1 which is the measured value for Na^+ for an infinite dilute solution at 22°C, and using our experimental results we obtain $l = 22\,\mathrm{nm}$.

This value corresponds to the minimum size of a simple dumbbell structure predicted by Kerr effect experiments [7]. It is possible to consider that the nano-droplets although connected by gelatin bridges act as 'isolators' for the movement of ions. In this way even in the presence of a large interconnected network the units that contribute to the dielectric properties have a finite length.

CONCLUSIONS

There are many different experimental data (conductivity, viscosity, neutron diffraction, light scattering and Kerr effect) which have been obtained on the same system. It is evident that, when a certain gelatin concentration is attained, a high connectivity structure is arranged. This kind of behavior has been described as a typical percolative one (formation of an "infinite cluster"). While, a difference between the dielectric behavior before and after the same gelatin range concentration is observed there is not, such a neat difference as that observed with other experimental techniques. We have calculated the electrical path length. There is, at least qualitatively, a good agreement between results from Kerr effect experimental results and ours. Nevertheless, it must be pointed out that only one of these elementary structures ("dumbbells" type) significantly contributes to the permittivity. On the other hand, time relaxation measurements have been recently performed in organogels based in a water/*n*-heptane AOT and gelatin [12]. The authors pointed out that the permittivity follows a similar behavior to that described in this paper, but no microscopical mechanism is proposed, although the Atkinson, Robinson's *et al.*, model is admitted without further justification. In our opinion, the problem of the organogel-based microemulsion structure is an open question, because neither the experimental data nor the theoretical analysis allows this question to be solved without ambiguity.

References

[1] Langevin, D. (1986). *Mol. Cryst. Liq. Cryst.*, **136**, 259.
[2] Luisi, P. L., Scartazzini, R., Haering, G. and Schurtenberg, P. (1990). *Colloid Polym. Sci.*, **268**(4), 356.
[3] Quellet, C. and Eicke, H. F. (1986). *Chimia*, **40**, 223.
[4] Petit, C., Zemb, Th. and Pileni, M. P. (1991). *Langmuir*, **7**, 223.
[5] Hinze, W. L., Uemasu, I., Dai, F. and Braun, J. M. (1996). *Current Opinion in Colloid and Interface Science*, **1**(4), 502.
[6] Feldman, Y., Zuev, Y., Polygalov, E. and Fedotov, V. (1992). *Colloid < Poly. Sci.*, **270**, 768.
[7] Acosta, E., Kurlat, D. H., Bisceglia, M., Ginzberg, B., Baikauskas, L. and Romano, S. D. (1996). *Coll. and Surf.*, **106**, 11.
[8] Capitani, D., Segre, A. L., Haering, G. and Luisi, P. L. (1988). *J. Phys. Chem.*, **92**, 3500.
[9] Atkinson, P. J., Grimson, M. J., Hennan, R. K., Howe, A. M. and Robinson, B. H. (1989). *J. Chem. Soc. Chem. Commun.*, p. 1807.

[10] Hill, N., Vaughan, W. E., Price, A. H. and Davies, M. (1969). "Dielectric Properties and Molecular Behaviour", van Nostrand (London), p. 374.
[11] Shwartz, G. J. (1962). *J. Phys. Chem.*, **66**, 2637.
[12] Aliotta, F., Arcoleo, V., La Manna, G. and Turco Liveri, V. (1996). *Coll. Polym. Sci.*, **274**(10), 989.