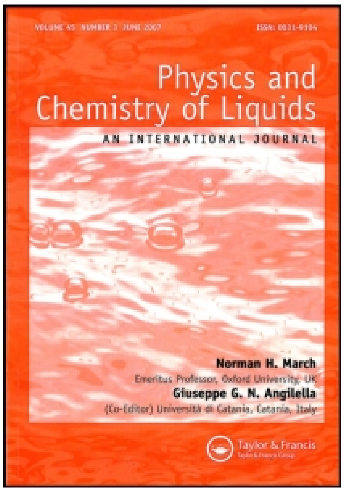

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LETTER
Does the Electrical Conductivity of W/O Microemulsions follow a Percolative Behaviour?

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The conductivities of different microemulsions prepared with triethanolamine were measured as a function of concentration for several temperatures. The goal of this work has been to test the degree of accuracy of the application of the scaling laws used in the literature. Our conclusion is that there is no general validity even though the abrupt variation of conductivity with concentration may be seen as a percolative phenomenon.

KEY WORDS: Scaling laws, percolation.

1. INTRODUCTION

It's well known from the experimental point of view, that the electrical conductivity (σ) of w/o microemulsions increases steeply when the concentration of the dispersed phase exceeds a certain threshold value. A similar behaviour has also been noticed in other condensed matter systems, as sheets of colloidal graph paper with holes punched in it, amorphous materials, powder semiconductors, conductor and insulator sphere mixtures, etc. These latter phenomena have been studied theoretically within the frame of the percolation theory and scaling laws (Kirkpatrick 1973); (Stauffer 1985). Then, it's natural to consider the same theory to give account of microemulsion data, and this has indeed been done by several authors. Nevertheless, it must be pointed out that the analysis of the experimental data has a strong dependence on the author's approach to the subject. In the literature (Lagourette, Peyrelasse, Boned and Clausse 1979); (Boned, Clausse, Lagourette, Peyrelasse, McClean and Sheppart 1980); (Lagües, Ober and Taupin 1987); (Lagües and Sauterey 1980); (Fang and Venable 1987); (Moha-Ouchane, Peyrelasse and Boned 1987), the well known scaling laws

$$\begin{aligned} &\sigma \sim (\phi^c - \phi)^{-s} \qquad \text{if } \phi < \phi^c \\ &\sigma \sim (\phi - \phi^c)^t \qquad \text{if } \phi > \phi^c \end{aligned} \tag{1}$$

have been considered, being ϕ the water volume fraction and ϕ^c its threshold value. The values of the critical exponents t and s proposed by the mentioned authors are: t = 1.6; 1.94; s = 1.2. Others, don't give explicit values of t and s, even though they admit a percolative mechanism (Cazabat, Chatenay, Langevin and Meunier 1982); (Cazabat 1985); (Langevin 1986). Besides, Scriven (Davis, Scriven, Miller, Prager and Makosco 1981); (Kaher, Bennet, Davis and Scriven 1983) applies the scaling laws to the $W_I \rightarrow W_{III}$ transition, involving an approach which is different from all the others.

Moreover, it's not apparent whether the critical exponents should be obtained through the analysis of $\sigma = f(\phi)$ or $\sigma_r = f(\phi)$, σ_r being the reduced electrical conductivity, computed as the ratio σ/σ_{NaCl} where σ_{NaCl} is the conductivity of the brine used to prepare the microemulsion.

Finally, a well defined value of ϕ^c must be found in order to be able to confidently verify the scaling laws. A review of the results set forth in the previously mentioned papers, doesn't show that the value of ϕ^c is always unambiguously determined, and this makes the calculation of the critical exponents quite uncertain.

This situation leaded us to perform a careful measurement of $\sigma = f(\phi)$ in w/o microemulsions as well as to study critically the experimental data we obtained.

2. EXPERIMENTAL

The conductivity was measured on samples prepared with dodecane, brine (with different ClNa concentrations), triethanolamine sulfonate dodecylbenzene (surfactant) and normal amyl alcohol (cosurfactant). Six series of microemulsions were obtained, each characterized by different concentrations of these components, and with a wide range of brine concentrations leading to the formation of Winsor II (w/o) microemulsions up to the limit of the Winsor III type. The tubes containing the liquid systems were introduced into a thermostatic bath to obtain thermal stability. The different temperatures (20.1; 25; 26.7; 28 and 28.7°C) were controlled within 0.1°C. The measurements were carried out by introducing a Metrohm AG cell ($c = 0.082\,\mathrm{cm}^{-1}$) calibrated using KCl solutions into the upper phase (microemulsion), without separating it from the lower aqueous phase, in order to avoid any possible phase separation while measuring. We used a General Radio Type 1656 Bridge, working at 1 kHz.

Figure 1 represents the variation of log σ versus ϕ for Series I and $T = 28.7°C$. The data corresponding to the other series and temperatures were also represented, displaying ten curves similar to the one shown. In agreement with the previously mentioned authors, two well-defined zones were observed: a very low conductivity one—for low water concentrations—and other, when ϕ exceeds a certain value, where the conductivity increases steeply, varying its value up to three orders of magnitude. But the definition of this threshold value ϕ^c turns out to be ambiguous and elusive when analyzing the shape of the experimental curves, thus leading to a dubious choice.

Consequently, several criteria were formulated to allow a definition of ϕ^c and test the validity of the scaling laws.

Following Moha-Ouchane (1987), if the choice of ϕ^c is made as the value that maximizes $d(\log \sigma)/d\phi = f(\phi)$, a remarkable indefinition is found because in most of our curves the slope is almost constant while ϕ varies widely.

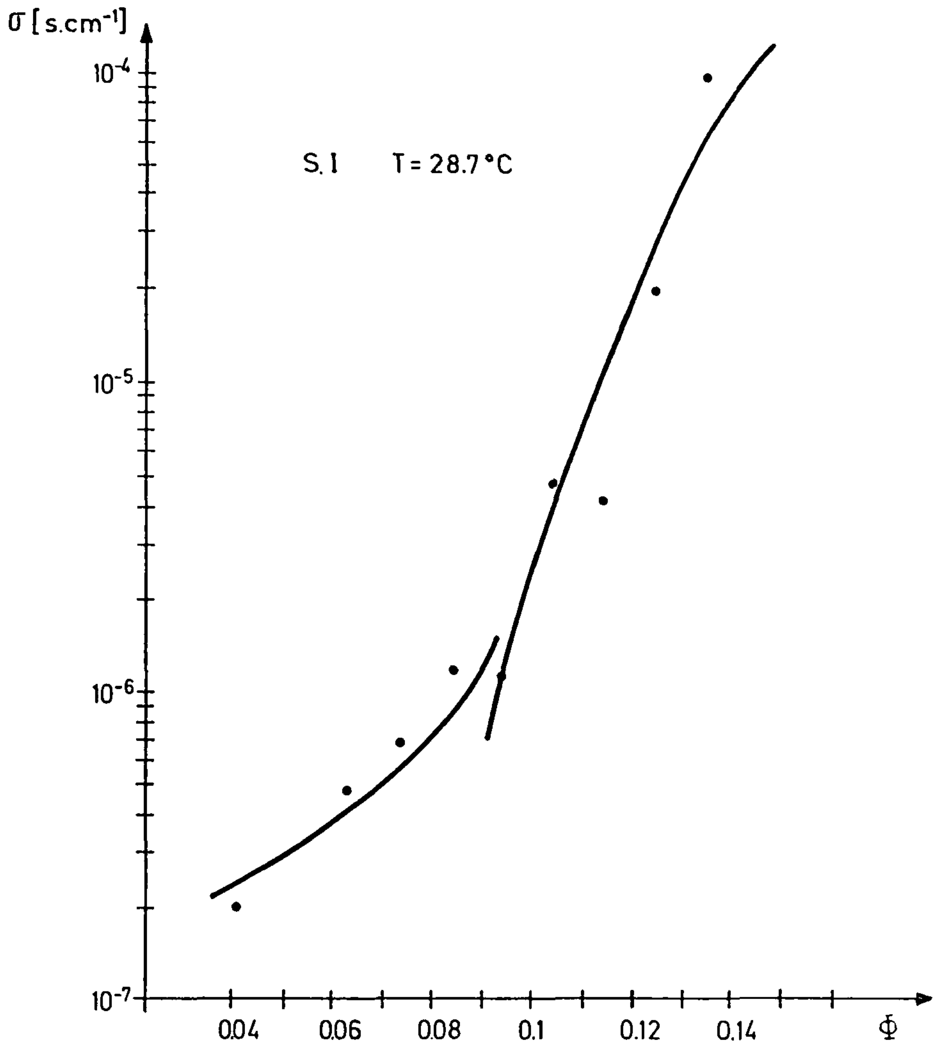

Figure 1 Logarithmic variation of electrical conductivity σ (S.cm^{-1}) vs. water volume fraction ϕ, for Series I and T = 28.7°C.

A different analysis we performed consists in studying the agreement between the experimental plots log $\sigma = f(\phi)$ and the theoretical curves obtained giving different arbitrary values of ϕ^c (near the probable threshold) to the expression (1). The values of the calculated critical exponents t and the corresponding correlation coefficients r were represented versus ϕ^c. Figure 2 shows this for Series I, T = 28.7°C. The linear correlation is found to be mostly greater than 0.95, while t varies substantially. The next step is to choose the "right" ϕ^c. The following somewhat arbitrary criterion could be proposed: to choose ϕ^c as the value that corresponds to the maximum of the correlation coefficient r. In the case of Figure 2, the application of this criterion leads

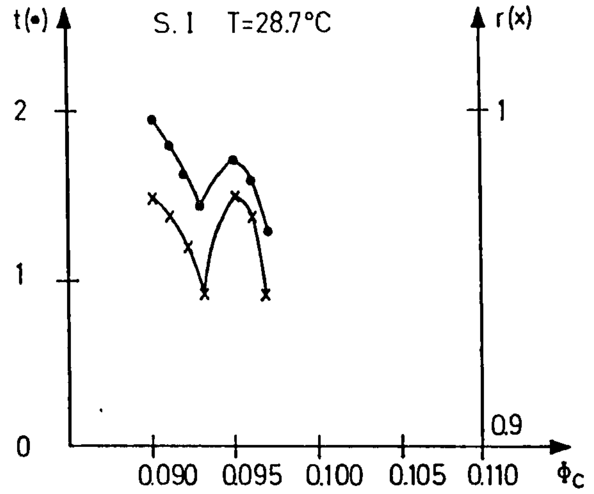

Figure 2 Calculated critical exponent t and correlation coefficient r corresponding to the adjustment of log $\sigma = f(\phi)$ with Eq. (1), vs. arbitrarily given values of ϕ^c.

to: $\phi^c = 0.095$; $t = 1.73$; $r = 0.97$. The results for other series and temperatures are displayed in Table 1. Even though these values are in good agreement with those presented by other authors for similar systems, this method of analysis lacks generality, because some series of microemulsions have been found for which $r = f(\phi^c)$ doesn't show a maximum, thus remaining uncertain the choice of the threshold ϕ^c. Moreover, this method makes apparent the fact that different choices of the threshold value—even within a narrow interval—lead to quite different values of the critical exponent t, and this suggests that it might be possible to adjust the parameters in order to obtain the results expected beforehand.

We have also considered another criterion, based on the experimental measurement of ϕ in the microemulsion as a function of the initial concentration of NaCl in the brine. When plotting the results, a change of slope is noticed in the curves, which takes place for a certain percentage of NaCl. This percentage is in correspondence with a value of ϕ which could be considered as the threshold value. Performing this analysis some agreement is found with the values in Table 1; but the greatest agreement between this analysis and the previous ones lies on the unavoidable ambiguity to define the threshold value, due to the fact that the mentioned change of slope is not sharp enough to make sure that this threshold exists.

To go further in this discussion, we have calculated the reduced conductivities σ_r for every sample and temperature measured. Figure 3 represents the variation of log σ_r versus ϕ and includes data of the different microemulsion series and temperatures. It may be concluded that the complete set of data corresponds to a common phenomenon, which could be described, but not without ambiguity, using the scaling laws (1). Doing so, calculations using the maximum r criterion yield: $\phi^c = 0.1$; $t = 2$ and $r = 0.9$ for $\phi > \phi^c$, and for $\phi < \phi^c$ fairly good agreement is found with $s = 1.2$.

Table 1 Values of the threshold water volume fraction ϕ^c as chosen using the maximum correlation criterion, and the corresponding values of the critical exponent t and correlation coefficient r for several series of microemulsions and different temperatures.

Series	*T(°C)*	ϕ^c	*t*	*r*
I	20	0.07	1.23	0.92
I	28.7	0.095	1.73	0.97
II	20	0.11	1.64	0.99
II	26.7	0.106	1.61	0.99
II	28.7	0.12	1.97	0.98
III	20.1	0.145	1.42	0.99
III	25	0.092	2.26	0.99
IV	28	0.125	2.43	0.99
V	28	0.114	2.01	0.99
VI	20.1	0.135	1.63	0.99

Nevertheless, once more it is clear that not only it is possible to adjust the experimental data with other parameters in these scaling laws, but also that different laws could be found to give an agreement as good as the one obtained, thus subsisting the already noted ambiguity.

Summing up, even though all these different ways of analyzing the experimental data show a clear distinction between the conductor behaviours of microemulsions for low and high concentrations, none of them evidences the existence of a well-defined water concentration threshold, but seemingly what is shown is a progressive, non-critical change. This fact makes dubious the application of simple scaling laws.

3. DISCUSSION

Independently of the precedent analysis, from the physical point of view we feel that the risk is run to oversimplify the problem if these phenomena are described as percolative processes ruled by simple scaling laws. Obviously, the first objection is that the plain percolation theory cannot be applied, because it's meant for a static lattice, while in the liquid state account must be given of brownian motion. Besides, $\sigma = 0$ for $\phi < \phi^c$ according to this theory. Lagües (Lagües *et al.* 1978, 1979, 1980) was the first in considering these critics when he introduced the concept of "stirred" percolation. He supposed that conduction should be due to diffusive movement for $\phi < \phi^c$ and, taking into account a previous work by De Gennes (De Gennes 1978) he postulated a critical exponent $s = 1.2$. For $\phi > \phi^c$ the process would be described by the usual percolation theory. The following objections to this approach can be stated:

—The time scales for atomic and electrical transport processes are quite different, and it isn't evident that they should be related according to the simple equations proposed by Lagües, which are derived from the Nernst-Einstein relations.

—The agreement between the theoretical value of the critical exponent t and the one found by Lagües could well be fortuitous or even could have been forced through

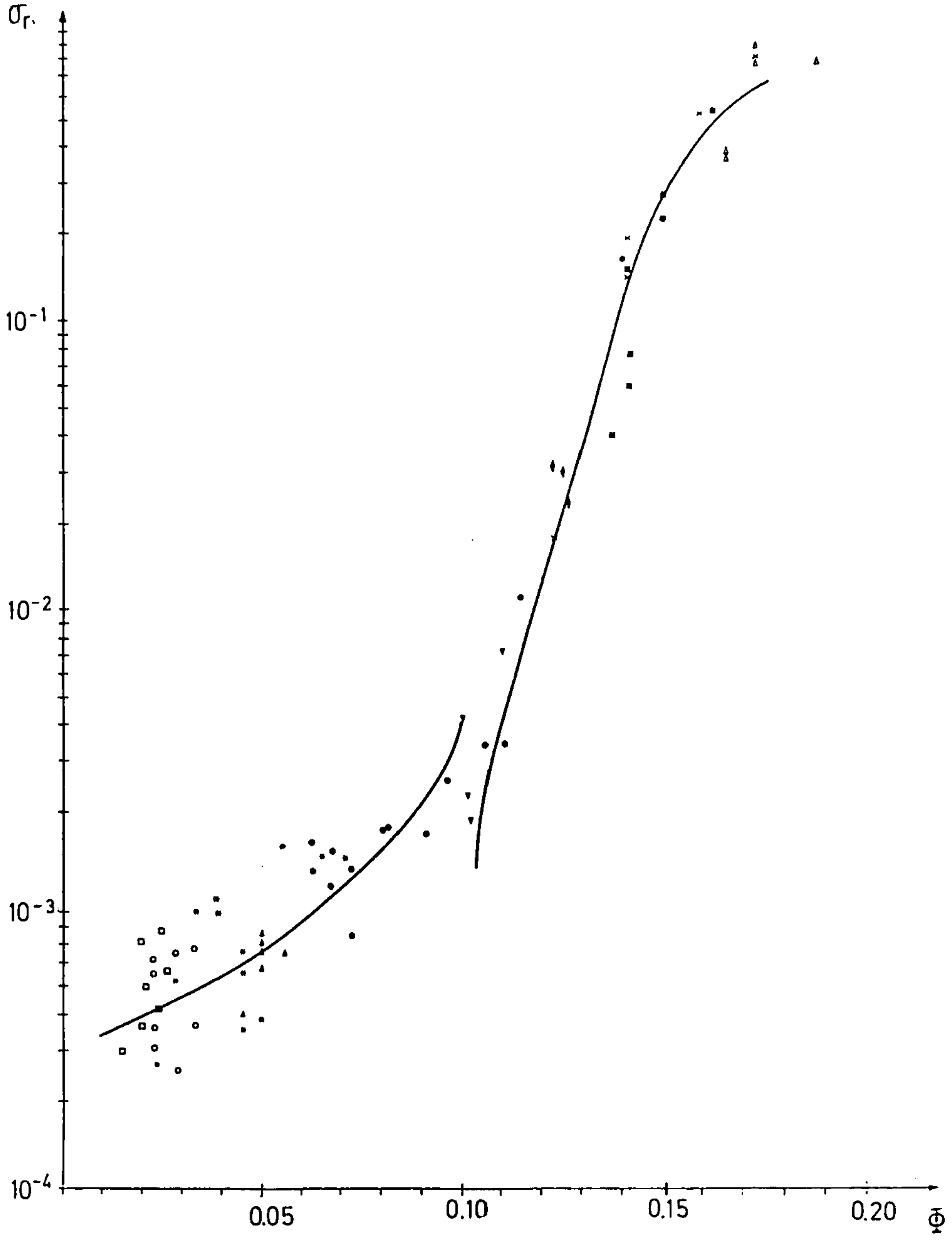

Figure 3 Logarithmic variation of the reduced conductivity σ_r vs. water volume fraction ϕ. *Series I; ● Series II; ▼ Series III; ■ Series IV; X Series V; ▲ Series VII; △ Series VIII; □ Series IX; ○ Series X.

some voluntary handling of the experimental data. We must point out in the measurements we performed we've found a good number of counter-examples.

—The hypothesis of rigid spheres is too simple a picture for these systems (Safran, Turkevich and Pincus 1984) and it disregards the mechanism of charge transport from one droplet to another during a "sticky collision" and the subsequent formation of a conductor path (Cazabat *et al.* 1982, 1985); (Langevin 1986).

The analysis presented by Grest (Grest, Webman, Safran and Bug 1986) doesn't differ from that of Lagües' in what concerns the physical hypothesis.

Therefore, we can say that in the present state of the theory, there are no valid reasons to induce us to accept that the conductivity should follow simple scaling laws similar to those applied in the study of critical phenomena.

Still, the discussion is open concerning the "geometric" approach of the percolation theory, that is: when the water volume fraction in a microemulsion is enough for a cluster to form throughout the sample, the conductivity rises abruptly. Now, as the volume of brine in the microemulsion increases, so does the number of paths available for the charge to be conducted. In the limit, the maximum conductivity would be obtained if we'd have a solution formed only by the "active" centers, that is, the salt solution used to formulate the microemulsion in the same conductions of salt concentration and temperature. Here's the reason why the reduced conductivity curve is enlightening, as it allows us to compare the different charge transport abilities of the systems, independently of the maximum conductivity each of them might have. This leads us to consider that the main factor to pay attention to, is the geometric distribution of active centers. This point of view is supported by the fact that ϕ increases when the initial salt concentration decreases, and nevertheless σ rises appreciably. The reduced conductivity plot shows that the values—corresponding to different series and temperatures—lie on a common curve, leading to conclude that the main factor to determine the conductivity is the formation of connective paths, regardless of the system considered. Besides, as this representation may be described using critical exponents similar to those established in the frame of the percolation theory, we conclude that this theory gives a correct qualitative description of the phenomena studied, leaving only as an open question the type of mathematical law that rules them.

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