

## Viscosity and the phenomenon of percolation in microemulsions

J. Peyrelasse, M. Moha-Ouchane, and C. Boned

Université de Pau et des Pays de l'Adour, Centre Universitaire de Recherche Scientifique, Laboratoire de Physique des Matériaux Industriels, Avenue de l'Université, 64000 Pau, France

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The viscosity of water/AOT/oil microemulsions (undecane, isooctane, cyclohexane) has been studied as a function of the molar ratio  $n = [\text{water}]/[\text{AOT}]$  and the volume fraction  $\phi$  (water + AOT) at  $T = 25^\circ\text{C}$ . [Here AOT is an abbreviation for sodium bis(2-ethylhexyl)sulfosuccinate.] At constant  $\phi$  and variable  $n$ , the presence of a maximum viscosity can be observed. The results are discussed in connection with a percolation model and a very good qualitative agreement is obtained. The results are compatible with those obtained previously on the conductivity and complex permittivity of these microemulsions. The results show the importance of the idea of "percolation threshold lines." Emphasis is placed on the importance of interactions and on the necessity of following an experimental procedure involving constant interaction (for either ternary or quaternary systems).

### INTRODUCTION

Five years ago, Angel *et al.*<sup>1</sup> stressed the significance of studying the three-component microemulsions (without alcohol) and agreed that studying four- or five-component systems (brine) leads to theoretical and experimental difficulties, hindering progress in the understanding of the properties of such systems. It has long been known that sodium bis(2-ethylhexyl) sulfosuccinate (AOT) allows high water-in-oil solubility without adding any other components. Surfactants other than AOT also have this property, and the amount of research on ternary systems has grown considerably within the last 5 years. It is well known that for AOT-oil-water systems at low and intermediate water concentrations, the microemulsions consist of water-in-oil globules which undergo Brownian motion. The globules also show attractive interactions<sup>2</sup> that increase linearly with the molar ratio  $n = [\text{water}]/[\text{AOT}]$  and with the radius of the globules.

A large electrical conductivity transition has been observed in several water-in-oil systems.<sup>3-11</sup> As the volume fraction of water or temperature increases, the electrical conductivity increases sharply by several orders of magnitude. Several publications<sup>7,8,10</sup> indicate that this is due to percolation of a phase of spherical globules in the continuum. A percolation model for the transition involves the formation of clusters of water globules sufficiently close to each other for the transfer of charge carriers between the globules to occur efficiently.<sup>12</sup> Similarly, the dielectric behavior of ternary systems of this kind is also explained by a percolation model.<sup>7,8,13,14</sup> In two previous papers<sup>11,14</sup> we studied the conductivity and permittivity of various water/AOT/oil systems. We showed that they obey the percolation law

$$\frac{\epsilon^*}{\epsilon_1^*} = |\phi - \phi_c|^\mu f \left[ \frac{\epsilon_2^*/\epsilon_1^*}{|\phi - \phi_c|^{\mu+s}} \right], \quad (1)$$

where  $\epsilon^*, \epsilon_1^*, \epsilon_2^*$  are the complex permittivities of the mi-

croemulsion and the components.  $\phi$  is the volume fraction (water + AOT) of the dispersed phase, and  $\phi_c$  is the percolation threshold value. We used  $\mu = 1.94$  and  $s = 1.2$  which expresses the dynamic aspect of the phenomenon.<sup>4,15</sup> We carried out a systematic investigation as a function of molar ratio  $n$ , temperature, and salt content. The results plotted in the ternary diagram show a percolation threshold line (at fixed temperature). In fact, because of the phenomenon of hopping, we define  $\phi_{cc}$  as the percolation threshold for conductivity and  $\phi_{cd}$  as the percolation threshold for permittivity.<sup>14</sup> Figure 1 is an example of the results obtained.

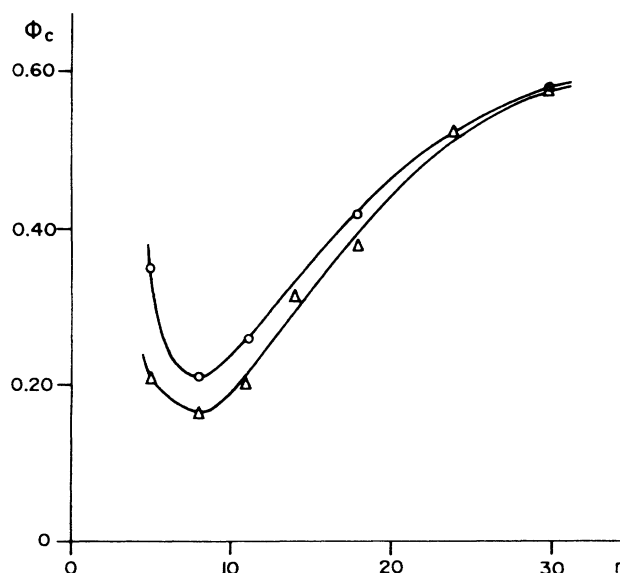


FIG. 1. Water/AOT/undecane systems ( $T = 15^\circ\text{C}$ ). Variation of the percolation threshold vs  $n$ . O: values for  $\phi_{cd}$  determined with static permittivity.  $\Delta$ : values for  $\phi_{cc}$  determined with conductivity (from Ref. 14).

The phenomenon of percolation, which is observed very clearly for conductivity and permittivity, must be involved in other physical properties. In this paper, we present the results obtained for viscosity of water/AOT/oil systems.

### EXPERIMENTAL TECHNIQUE

Measurements of viscosity were carried out using the standard capillary viscosimeter method (Viscotimer Lau-da S/1). During measurement, the viscosimeter is placed in a bath thermostatted at  $0.1^\circ\text{C}$ . The dynamic viscosity  $\eta$  is deduced from the kinematic viscosity data by multiplying the result by the specific gravity of the sample under study. The specific gravity was measured using a DMA Anton Paar K. G. automatic densimeter also thermostatted at  $0.1^\circ\text{C}$ . Measurement of the specific gravity was carried out with an absolute uncertainty lower than  $10^{-3}\text{ g/cm}^3$ . Consequently, relative uncertainty for the dynamic viscosity  $\eta$  can be estimated to be less than 1%. We used cyclohexane (Fluka AG), isooctane (Fluka AG puriss), undecane (Fluka AG purum), and AOT (Fluka AG purum). All the samples are characterized by the volume fraction  $\phi$  (water+AOT) and the molar ratio  $n = [\text{water}]/[\text{AOT}]$ . All the experiments were conducted at  $25.0 \pm 0.1^\circ\text{C}$ .

### EXPERIMENTAL RESULTS

#### Study of dynamic viscosity at fixed $n$

At constant temperature and molar ratio,  $\eta$  is observed to increase with  $\phi$ . Figures 2 and 3 are characteristic. This result is well known and can also be observed with quaternary microemulsions. The reader will, for example, find similar experimental curves in Refs. 16–21.

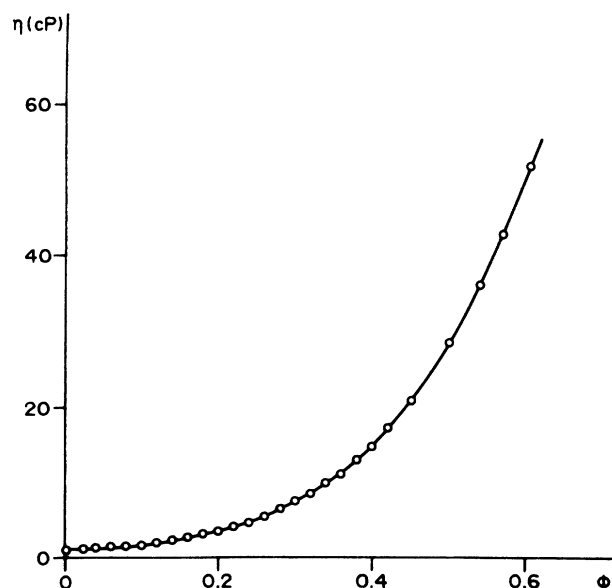


FIG. 2. Water/AOT/undecane system ( $T = 25^\circ\text{C}$ ;  $n = 25$ ). Variations of  $\eta(\text{cP})$  vs  $\phi$  are shown.

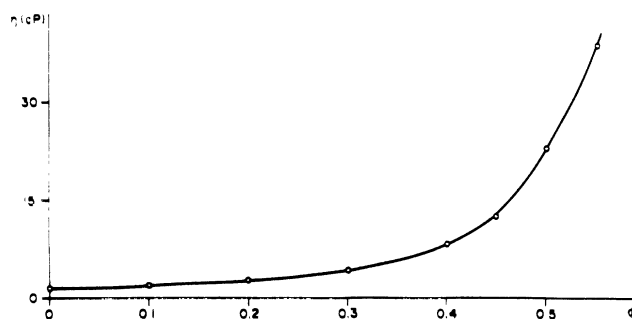


FIG. 3. Water/AOT/cyclohexane system ( $T = 25^\circ\text{C}$ ;  $n = 13$ ). Variations of  $\eta(\text{cP})$  vs  $\phi$  are shown.

#### Study of dynamic viscosity at fixed $\phi$

We also studied variations of dynamic viscosity versus molar ratio  $n$  for fixed values of  $\phi$  and  $T$ . Figures 4, 5, and 6 represent the results obtained for various conditions. Only one study was found in the literature presenting curves of viscosity variations versus molar ratio, namely the articles by Rouvière *et al.*<sup>22–24</sup> relating to the water/AOT/heptane and water/AOT/decane systems. The curves are very similar: maximum for  $n = 8$ , followed by a flattened minimum for  $n = 20$ . Moreover these curves show that the maximum decreases with in-

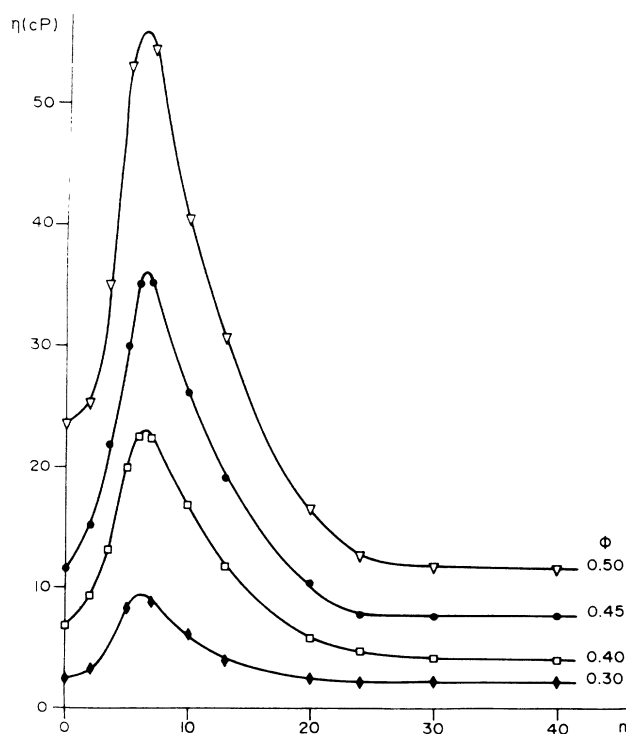


FIG. 4. Water/AOT/isooctane system ( $T = 25^\circ\text{C}$ ). Variations of  $\eta(\text{cP})$  vs  $n$  for different values of  $\phi$  are shown.

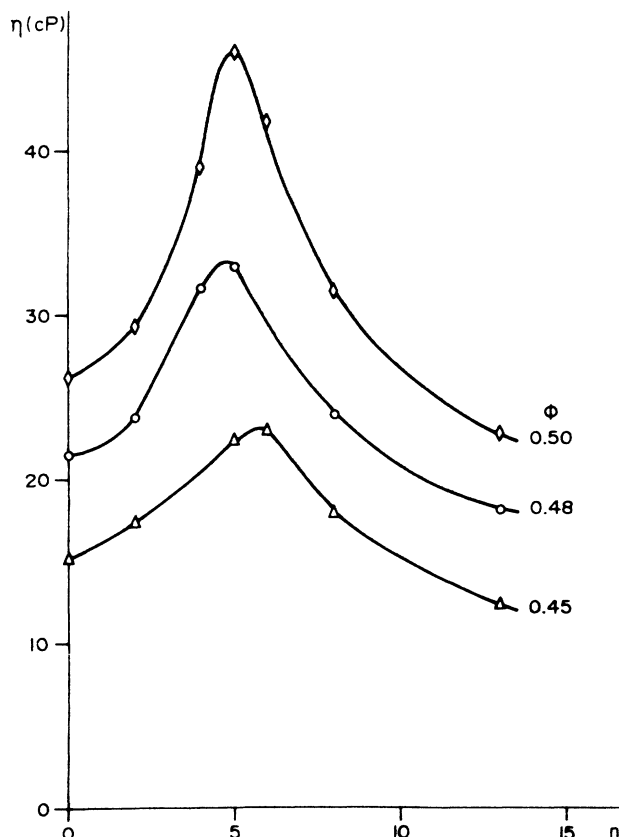


FIG. 5. Water/AOT/cyclohexane system ( $T=25^{\circ}\text{C}$ ). Variations of  $\eta(\text{cP})$  vs  $n$  for different values of  $\phi$  are shown.

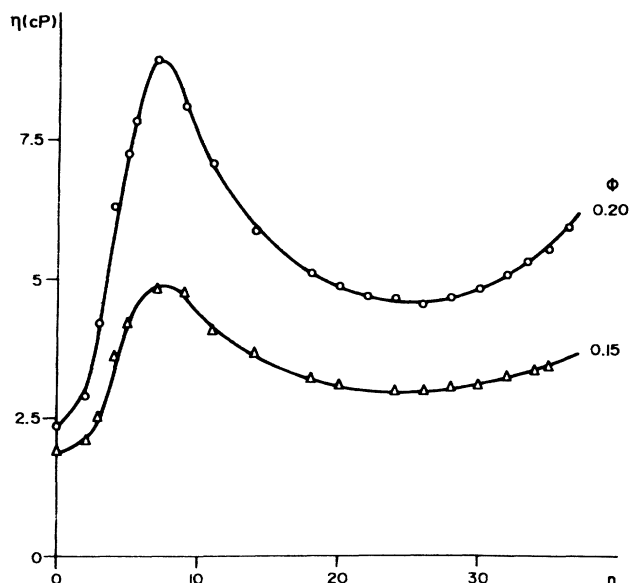


FIG. 6. Water/AOT/undecane system ( $T=25^{\circ}\text{C}$ ). Variations of  $\eta(\text{cP})$  vs  $n$  for different values of  $\phi$  are shown.

creasing salinity. Finally, we verified that whatever the values of  $\phi$  and  $n$ , the microemulsions present Newtonian character over a wide range of shearing rate.

## DISCUSSION

As a result of the phenomenon of percolation, conductivity and permittivity obey characteristic scaling laws. It can be shown that when in Eq. (1) the modulus of  $(\epsilon_2^*/\epsilon_1^*)/|\phi - \phi_c|^{\mu+s}$  is much smaller than 1, we obtain

$$\sigma = A(\phi_c - \phi)^{-s}, \quad \epsilon_s = A'(\phi_c - \phi)^{-s} \quad \text{if } \phi < \phi_c, \quad (2)$$

$$\sigma = B(\phi - \phi_c)^{\mu}, \quad \epsilon_s = B'(\phi - \phi_c)^{-s} \quad \text{if } \phi > \phi_c. \quad (3)$$

In reality, a maximum of  $(1/\sigma)(d\sigma/d\phi)$  as a function of  $\phi$ , and a maximum of  $\epsilon_s$  as a function of  $\phi$  are observed.<sup>14</sup> Since there is a percolation phenomenon, it might be thought that the viscosity must also present particular variations. A well-known example is the sol-gel transition which corresponds to the formation of a polymer by polyaddition of monomers. With time the viscosity increases and at time  $t_c$  a molecule of infinite length is formed.  $t_c$  corresponds to the gelation point, and, by analogy with Eqs. (2) and (3), we can write<sup>25</sup>

$$\eta \alpha (t_c - t)^{-s} \quad \text{if } t < t_c, \quad (4)$$

$$E \alpha (t - t_c)^{\mu} \quad \text{if } t > t_c. \quad (5)$$

$E$  is the elastic modulus. However, the critical exponent obtained for  $\eta$  can have various values. It depends on the experimental conditions (initial monomer concentration), which suggests the existence of different growth mechanisms for the polymer molecules.

As far as microemulsions themselves are concerned, one can refer to recent work carried out by Quemada and Langevin.<sup>26</sup> In particular, these authors studied variation of  $\eta$  with salinity during the transition Winsor I  $\rightarrow$  Winsor II  $\rightarrow$  Winsor III. They start out with Krieger's equation,

$$\eta = \bar{\eta}_F \left[ 1 - \frac{\phi_{\text{eff}}}{\phi_{\text{mo}}} \right]^q \quad (\phi_{\text{eff}} < \phi_{\text{mo}}), \quad (6)$$

where  $\bar{\eta}_F$  is the effective-medium viscosity of the continuous phase,  $q$  a critical exponent, and  $\phi_{\text{mo}}$  the effective packing volume fraction. Mention should be made of a very recent publication by Berg *et al.*<sup>27</sup> on viscosity of the water/AOT/decane system as a function of  $\phi$  and of temperature towards the critical point. As the system approaches the critical temperature from an initial low temperature there is a large and regular increase in the viscosity which may be linked to the percolationlike transition observed in electrical conductivity. At lower temperatures, the microemulsion can be considered simply as a number of noninteracting spheres suspended in decane. This result could usefully be compared with the similar observation that we made about the complex permittivity of microemulsions far from the percolation threshold.<sup>14</sup> This increase in viscosity is not completely consistent with either a simple electroviscous model or a simple clustering model. The authors said that a better microscopic theory of the percolation transition is needed to

make progress in fitting the viscosity anomaly. Finally, the viscosity increase in the vicinity of percolation transition has also been indicated in Refs. 28 and 29.

Equations (4), (5), and (6) correspond to scaling laws, but it is clear that viscosity-percolation theory is far less developed than complex permittivity percolation theory. However, by analogy with the previous equations we can write the following equations:

$$\eta = A_v (\phi_{cv} - \phi)^{-s_v} \quad \text{if } \phi < \phi_{cv} \quad (s_v > 0), \quad (7)$$

$$\eta = B_v (\phi - \phi_{cv})^{\mu_v} \quad \text{if } \phi > \phi_{cv} \quad (\mu_v > 0). \quad (8)$$

The equivalent Eqs. (2) and (3) are only valid for  $\sigma$  if  $\sigma_2/\sigma_1 \ll |\phi - \phi_c|^{\mu+s}$ , which can be achieved fairly simply because oil is practically an insulator and water has a high conductivity. For the dielectric constant  $\epsilon_s$  it was observed that the range of variation of  $\epsilon_s$  during the phenomenon of the percolation is fairly low.<sup>14,30</sup> This is due to the fact that the difference between the permittivity of water and that of oil is not very great. So the actual scaling regime may be quite small. As the viscosity of oil is not very different from that of water it is therefore reasonable to suggest that Eqs. (7) and (8) are only valid within a very narrow interval close to  $\phi_{cv}$ . In these conditions any attempt at quantitative analysis of relations (7) and (8) is illusory. Generalizing the proposal of Stauffer *et al.*<sup>31</sup> in the case of gelation, we suggest the following relationships to represent viscosity far from  $\phi_{cv}$ :

$$\eta = \sum_{k=1}^{\infty} A_{vk} (\phi_{cv} - \phi)^{-s_{vk}} \quad \text{if } \phi < \phi_{cv} \quad (9)$$

$$(s_{v1} > s_{v2} > \dots > s_{vn} > s_{v,n+1} > \dots > 0),$$

$$\eta = \sum_{k=1}^{\infty} B_{vk} (\phi - \phi_{cv})^{\mu_{vk}} \quad \text{if } \phi > \phi_{cv} \quad (10)$$

$$(0 < \mu_{v1} < \mu_{v2} < \dots < \mu_{vn} < \mu_{v,n+1} < \dots).$$

Equations (9) and (10) reduce to equations (7) and (8) when  $|\phi - \phi_{cv}|$  is sufficiently small. Using Eqs. (9) and (10), the experimental variations of  $\eta$  can be accounted for qualitatively.

Figure 2 represents the variations of  $\eta$  versus  $\phi$  for the water/AOT/undecane system ( $T = 25^\circ\text{C}$ ,  $n = 25$ ). We have numerically adjusted the experimental values using  $\log_{10}\eta = a\phi^4 + b\phi^3 + c\phi^2 + d\phi + e$  at 0.3% average deviation. Figure 7 shows the shape of variations of  $d(\log_{10}\eta)/d\phi$  versus  $\phi$ . The curve traced in an unbroken line corresponds to the values calculated with  $4a\phi^3 + 3b\phi^2 + 2c\phi + d$ , while the experimental points correspond to the numerical evaluation from the experimental values. The curve shows that  $d(\log_{10}\eta)/d\phi$  goes through a maximum, consistently with the similar behavior of conductivity observed for  $d(\log_{10}\sigma)/d\phi$ . It can be seen that the value of  $\phi_{cv}$  obtained in this way [maximum of the curve  $d(\log_{10}\eta)/d\phi$  for  $\phi_{cv} = 0.25$ ] is close to the value of  $\phi_{cc}$  obtained by studying conductivity (Fig. 4 of Ref. 11, and Ref. 16). The maximum of  $d(\log_{10}\eta)/d\phi$  [the point of inflexion on the  $\log_{10}\eta = f(\phi)$ ] is much less clearly marked than that of  $d(\log_{10}\sigma)/d\phi$  (Ref. 14, for example), since for the systems studied the viscosities of

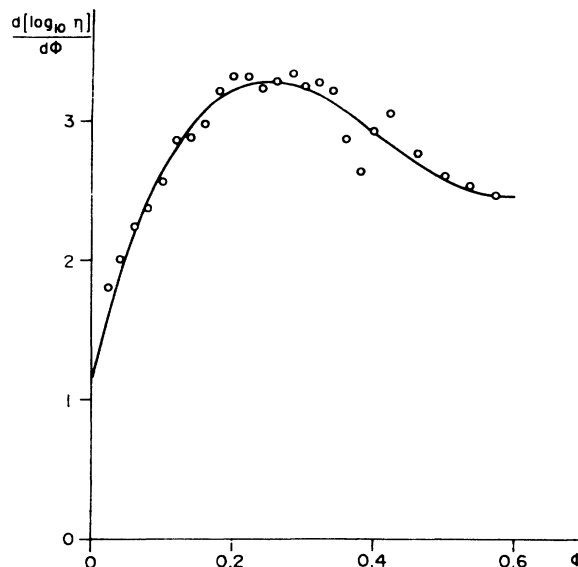


FIG. 7. Water/AOT/undecane system ( $T = 25^\circ\text{C}$ ;  $n = 25$ ). Variations of  $d(\log_{10}\eta)/d\phi$  vs  $\phi$  are shown.

oil and water are very close. The phenomenon is more marked when the viscosities of the two liquid phases are very different. As an example,<sup>32</sup> Figs. 8 and 9 represent the curves  $\log_{10}\eta = f(\phi)$  and  $d(\log_{10}\eta)/d\phi = f(\phi)$  for the waterless microemulsion glycerol/AOT/undecane studied at  $T = 25^\circ\text{C}$ . The sigmoid shape of the curve

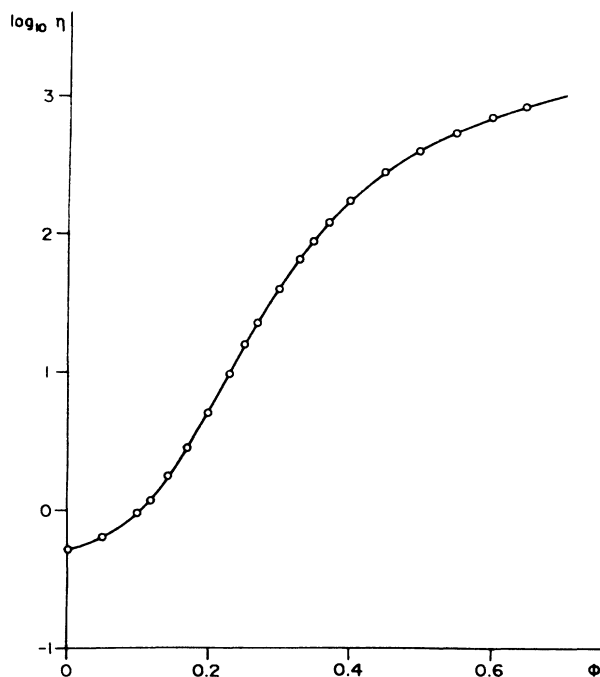


FIG. 8. Glycerol/AOT/isooctane system ( $T = 25^\circ\text{C}$ ; molar ratio  $[\text{glycerol}]/[\text{AOT}] = 3.2$ ). Variations of  $\log_{10}\eta$  vs  $\phi$  are shown.

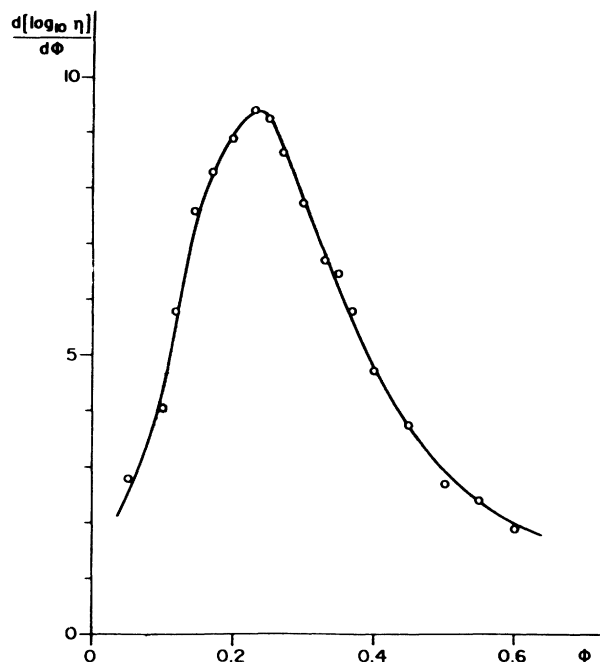


FIG. 9. Glycerol/AOT/isooctane system. ( $T=25^{\circ}\text{C}$ ; molar ratio [glycerol]/[AOT]=3.2.) Variations of  $d(\log_{10}\eta)/d\phi$  vs  $\phi$  are shown.

$\log_{10}\eta=f(\phi)$  is characteristic, and in this case  $d(\log_{10}\eta)/d\phi$  presents a marked maximum.

Equations (7), (8), (9), and (10) provide a qualitative explanation of the rapid increase of  $\eta$  with  $\phi$  when  $n$  is constant (Figs. 2 and 3). They also provide an explanation of the complex shape of curves of variations of  $\eta$  versus  $n$  when  $\phi$  is constant (Figs. 4, 5, and 6). This can be accounted for by the fact that it is mainly the variations in  $\phi_{cv}(n)-\phi$  which in this case determine the shape of the  $\eta(n)$  curves (for conductivity, it has been observed<sup>11</sup> that the prefactors  $A$  and  $B$  vary little with the molar ratio  $n$ ). One can draw an analogy with the equivalent curves  $\sigma(n)$  and  $\epsilon_s(n)$  (Refs. 11 and 14). Figure 10 illustrates this, and represents the variations of  $\eta(n)$  with the variations of  $\phi_{cv}$  considered as being equal to  $\phi_{cc}$ . Given the shape of the variations in  $\phi_{cv}(n)$ , there is a viscosity maximum at  $n=8$ , which corresponds to a minimum for  $\phi_{cv}$ . If  $\phi > \phi_{cv}(n)$ , then  $\phi - \phi_{cv}(n)$  is at a maximum for  $n=8$ , and according to Eqs. (8) and (10) the same is true of  $\eta$ . Similarly, if  $\phi < \phi_{cv}(n)$ , then  $\phi_{cv}(n)-\phi$  is at a minimum for  $n=8$ , and according to Eqs. (7) and (9) it follows that  $\eta$  is at a maximum. If there is an increase in  $\phi_{cv}$  with salinity (at constant  $n$  and  $\phi$ ), as is the case for  $\phi_{cc}^{II}$ , one can understand why the maximum for  $\eta$  decreases with increasing salinity, as Rouvière *et al.*<sup>23</sup> have observed. Similarly, when the temperature increases, an increase in the relative viscosity should be observed, since because of the deformation of the percolation thresholds line in the ternary diagram, the point representing the microemulsion moves from a zone in which  $\phi < \phi_{cv}$  to a zone in which  $\phi > \phi_{cv}$  (Refs. 11 and 14) (Fig. 11). This behavior has indeed been observed by other authors.<sup>27,28</sup> If one fol-

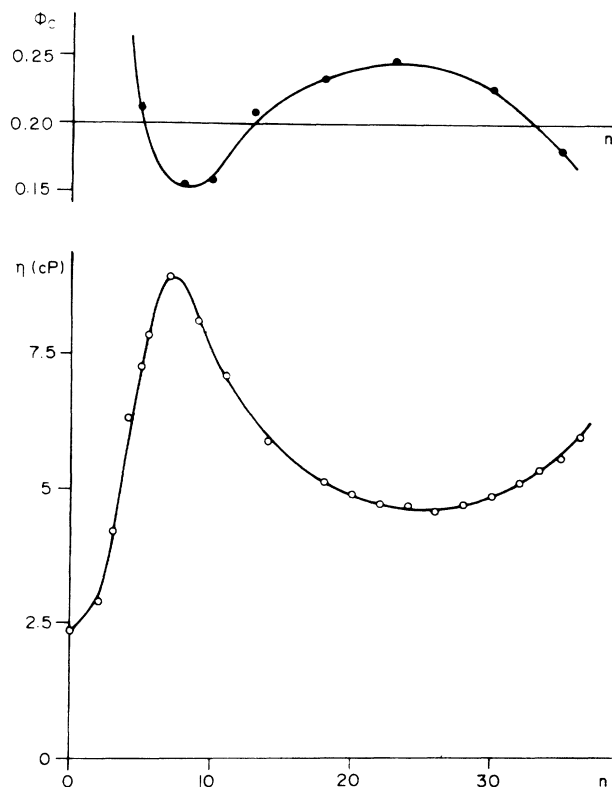


FIG. 10. Water/AOT/undecane system ( $T=25^{\circ}\text{C}$ ;  $\phi=0.2$ ). Variations of  $\eta(\text{cP})$  compared with variations of  $\phi_{cc}$  vs  $n$  are shown.

lows a line at either constant soap-oil ratio (Fig. 11, line  $B_1B_2$ ), or constant oil content (Fig. 11, line  $B'_1B'_2$ ), this can be accompanied by a decrease in conductivity and viscosity when water is added, an apparently paradoxical result, which has, however, been observed experimentally by Chen *et al.*<sup>33,34</sup> and verified more recently by Ninham

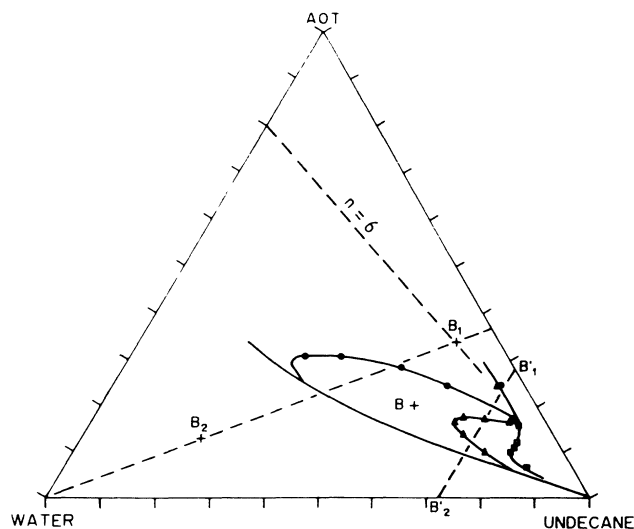


FIG. 11. Water/AOT/undecane system. Percolation threshold lines are shown. ●:  $T=15^{\circ}\text{C}$ ; ▲:  $T=25^{\circ}\text{C}$ ; ■:  $T=35^{\circ}\text{C}$  (from Ref. 11).

*et al.*<sup>35</sup> On the line  $B'_1B'_2$  (constant weight fraction of oil), it can be seen clearly that there can be an initial increase, followed by a decrease in the quantity measured when water is added.

### CONCLUSION

As with conductivity and permittivity, it appears that the shape of viscosity curves, and particularly those of the curve  $\eta(n)$ , can be interpreted, at least qualitatively, in the framework of the percolation theory. Certain apparently paradoxical results, obtained by other authors and reported above, can be given a clear interpretation within this theory.

As we have already said,<sup>14</sup> the accidents (maxima and minima) observed for water/AOT/oil microemulsions on experimental curves plotting conductivity, permittivity, and now viscosity, cannot be interpreted as involving structural modification. In particular, these maxima do not correspond to the presence of more or less elongated ellipsoids, as had been thought for static permittivity (these results are summarized in Ref. 14) and viscosity.<sup>22-24</sup> These accidents simply correspond to the fact that the distance  $|\phi - \phi_c|$  is maximal or minimal for the corresponding point on the ternary diagram.

This work and our previous articles<sup>11,14</sup> show that valid conclusions can be drawn from experimental measurements only if the experimental procedure followed is such that interaction between micelles remains constant. For ternary water/AOT/oil type systems, working at a constant molar ratio (which also keeps a constant radius) is enough. If the path followed does not correspond to a constant value for  $n$  (for example, lines  $B_1B_2$  and  $B'_1B'_2$  in Fig. 11), the term  $\phi_c$  in the quantity  $\phi - \phi_c$  varies at each point of the path followed and correct analysis of the re-

sults is consequently made very difficult. In that case, for want of a better solution, the maxima and minima observed for conductivity, permittivity, and viscosity can be associated with structural changes, which, according to analysis in terms of percolation, do not exist. It should be pointed out that working at constant interaction generally means working at constant temperature (interaction, and therefore  $\phi_c$ , generally vary with temperature). It is only if  $\phi_c(T)$  varies little with temperature (in other words if the interaction varies little) that analyzing the results with a scaling law involving  $|T - T_c|$  is satisfactory. In that case the exponents of the scaling laws are expected to be identical with those measured when the concentration of globules is varied.<sup>11,15</sup>

Finally this applies to quaternary systems as well as ternary systems. But in this case modifying variables at a constant interaction does not correspond to modifying variables at a constant water-soap ratio, because of the presence of alcohol. In general, in the phase tetrahedron, a constant interaction path is not located on a constant surfactant-alcohol ratio plane. The itinerary followed crosses several of these planes. Nevertheless it is easy to follow a constant interaction line for a quaternary system, operating by dilution for points located on the demixion line.

In conclusion, it seems to us that in order to fully understand the conductivity, permittivity, and viscosity of these systems one has to work at constant interaction, and therefore carry out a systematic study in the phase tetrahedron at each temperature, in particular with respect to molar ratio and volume fraction. The important parameter is the percolation threshold, and one needs to know the position in the phase tetrahedron of the threshold which corresponds to the relative interaction of the system studied.

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