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Dielectric relaxation and percolation phenomena in ternary microemulsions

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Dielectric relaxation of water/AOT/oil (iso-octane, undecane, dodecane, cyclohexane) microemulsions was studied by means of time-domain spectroscopy. [Here AOT is an abbreviation for sodium bis(2-ethylhexyl)sulfosuccinate.] The experiments were carried out for several values of the volume fraction ϕ (water + AOT) and of the molar ratio $n =$ [water]/[AOT]. They showed the presence of a maximum of static permittivity ϵ_s associated with a minimum of the relaxation frequency ν_R and a maximum of the frequency-spread parameter α. The influence of the salt content was also considered. The results are discussed with reference to the theory of percolation, and were found to be in close agreement with the theoretical predictions. By analogy with previous results on conductivity [M. Moha-Ouchane, J. Peyrelasse, and C. Boned, Phys. Rev. A 35, 3027 (1987)], the influence of temperature is discussed. The important part played by interactions and the phenomenon of "hopping" are demonstrated in connection with an already existing model (an off-lattice simulation). Finally, the results show the importance of the notion of "percolation threshold lines" introduced previously (Moha-Ouchane, Peyrelasse, and Boned).

I. INTRODUCTION

In a previous article[1] we studied the conductivity of the water-AOT-undecane system [AOT is an abbreviation for sodium bis(2-ethylhexyl) sulfosuccinate]. We showed that it obeyed the percolation laws

$$\sigma \propto (\phi-\phi_{cc})^{\mu} \text{ if } \phi>\phi_{cc} , \tag{1}$$

$$\sigma \propto (\phi_{cc}-\phi)^{-\bar{s}} \text{ if } \phi<\phi_{cc} , \tag{2}$$

where σ is conductivity, ϕ the volume fraction (water+AOT), and ϕ_{cc} the percolation threshold value. We used $\mu=1.94$ and $\bar{s}=1.2$ which expresses the dynamic aspect of the phenomenon.[2] We carried out a systematic study as a function of molar ratio $n=$[water]/[AOT], of temperature, and of the water/salt content. The results plotted in the ternary diagram show a line of percolation thresholds. Figure 1 displays the results obtained. At a given temperature the threshold line divides the realm of existence of the microemulsion into two area: (C) where $\phi>\phi_{cc}$ and where the system is therefore highly conducting, and (NC) where $\phi<\phi_{cc}$ and the system is then a poor conductor. Similarly, at fixed temperature and molar ratio, the threshold value increases with salt content.

The phenomenon of percolation, very clearly observed for conductivity, must also be involved for other physical properties. When we made conductivity measurements on the water/AOT/undecane system we sometimes also measured dielectric relaxation, at the same time and for the same samples. In this paper we will present both these results, and those obtained later on for other systems: water/AOT/cyclohexane, water/AOT/dodecane, and water/AOT/iso-octane.

II. EXPERIMENTAL PROCEDURE

Techniques for measuring dielectric properties by time-domain spectroscopy have been recently developed and present several advantages compared with conventional measurements in the frequency domain. Firstly, the method is fast; a complete dielectric relaxation spectrum can be obtained in only a few minutes. Secondly, the large number of experimental values obtained enables the relaxation domain to be plotted with an excellent definition.

The development of our experimental apparatus has already been reported in two technical articles.[3,4] It is a compact Tektronic WP 1200 unit with a reflectometer and a digital processing oscilloscope monitored by a calculator. Precise determination of the complex permittivity ϵ^* is possible as long as $\sigma<10^{-2}\,\mathrm{S\,m^{-1}}$. Studying alcohols with well-known properties, we verified that the relative uncertainty on ϵ' and ϵ'' ($\epsilon^*=\epsilon'-j\epsilon''; j^2=-1$) is about 3%. A low-frequency study of static permittivity was carried out with a Hewlett-Packard 4192A impedance meter monitored by the calculator. Using a Wayne-Kerr B331 autobalance precision bridge and Mullard platinated cells (Philips), determination of low-frequency electrical conductivity was carred out at 1.592 kHz.

We used cyclohexane (Fluka AG), iso-octane (Fluka AG puriss), undecane (Fluka AG purum), dodecane (Fluka AG purum), and AOT (Fluka AG purum). In some cases we used solutions of sodium chloride (Prolabo Norma pur). All samples are characterized by the volume fraction ϕ (water and AOT) and by the molar ratio $n=$[water]/[AOT]. All the experiments were carried out at 25.0±0.1 °C, unless otherwise indicated.

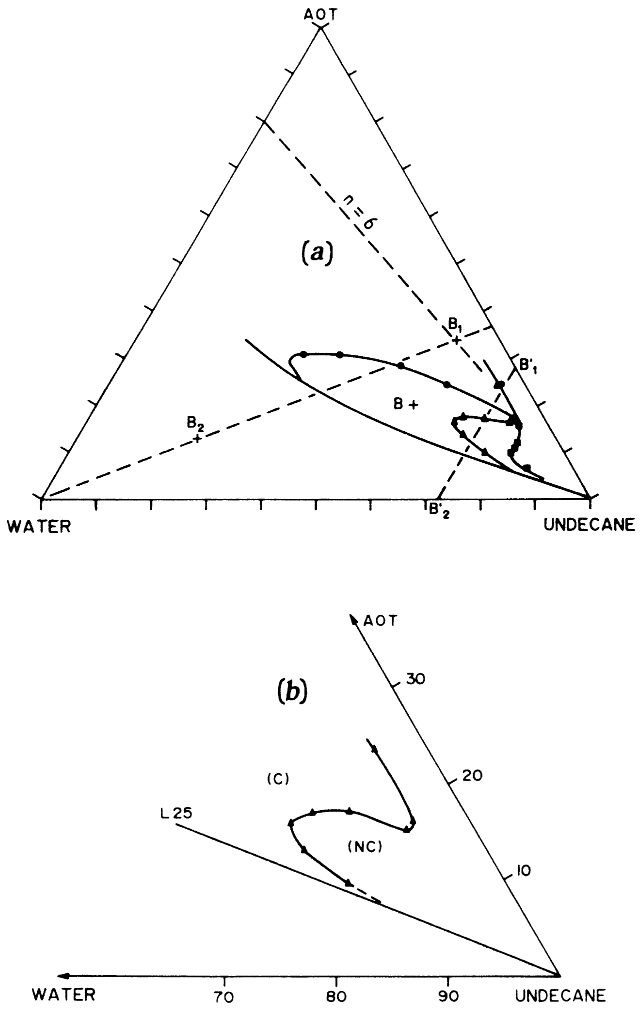

FIG. 1. (From Ref. 1.) (a) Water/AOT/undecane system. Percolation threshold lines. ●, $T=15\,^{\circ}\mathrm{C}$; ▲, $T=25\,^{\circ}\mathrm{C}$; ■, $T=35\,^{\circ}\mathrm{C}$. (b) Water/AOT/undecane system. Percolation threshold lines at $T=25\,^{\circ}\mathrm{C}$.

III. EXPERIMENTAL RESULTS

A. General observations

For all the samples studied we noted that all the microemulsions present not only overall conductivity but also a dielectric relaxation. Consequently, the complex permittivity $\epsilon^*(\omega)$ ($\omega=2\pi\nu$, where ν is frequency) can be expressed as $\epsilon^*(\omega)=\epsilon_R^*(\omega)-j\sigma/\epsilon_0\omega$, where ϵ_0 is the permittivity of a vacuum and $\epsilon_R^*(\omega)=\epsilon'(\omega)-j\epsilon_R''(\omega)$ represents the relaxation term. When $\sigma\leq10^{-2}$ S m^{-1} our apparatus can measure $\epsilon^*(\omega)$, but beyond this value it can only determine the static permittivity ϵ_s. For all the microemulsions we were able to study, the curve $\epsilon_R''(\omega)=f[\epsilon'(\omega)]$ is a semicircle centered under the ϵ' axis. Furthermore, the distribution of relaxation times shows that the relaxation observed satisfies the Cole-Cole empirical equation whatever the nature of the oil, the volume fraction, the molar ratio, and the salt content. So one can write

$$\epsilon_h^*(\omega)=\epsilon_h+\frac{\epsilon_s-\epsilon_h}{1+(j\nu/\nu_R)^{(1-\alpha)}} . \qquad (3)$$

ϵ_h is the permittivity when $\omega\rightarrow\infty$, ν_R is the frequency of

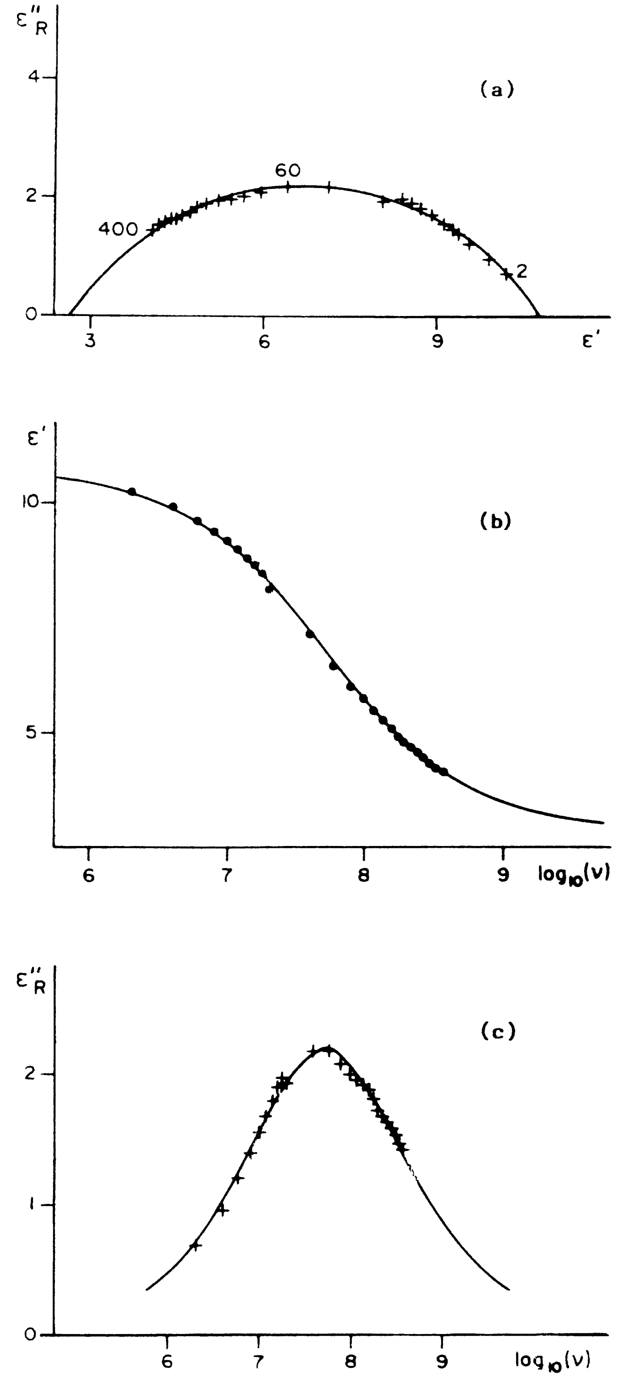

FIG. 2. Water/AOT/undecane system ($\phi=0.20$, $n=12$, $T=25\,^{\circ}\mathrm{C}$). (a) $\epsilon_R''(\epsilon')$ curve. Frequencies are in MHz. (b) Variations of ϵ' vs frequency (Hz). (c) Variations of ϵ_R'' vs frequency (Hz); ——, curves calculated using Eq. (3) with $\epsilon_s=10.77$, $\epsilon_h=2.65$, $\nu_R=53.42$ MHz, and $\alpha=0.365$.

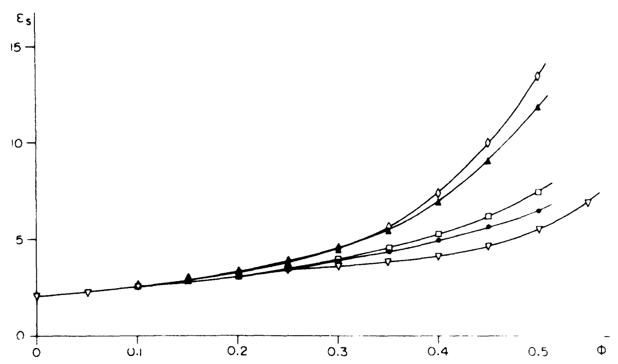

FIG. 3. Water/AOT/cyclohexane system ($T=25\,^{\circ}\mathrm{C}$). Variations of ϵ_s vs ϕ for different values of n. ∇, 2; ◇, 5; ▲, 8; □, 13; ●, 16.

the maximum absorption, and α is the frequency spread parameter. Figure 2 is a characteristic example. One can observe the excellent agreement between the experimental values and the values calculated from the Eq. (3). The reader can also refer to a previous paper[5] concerning the water/AOT/dodecane system, and a more recent paper concerning other systems.[6]

B. Influence of the volume fraction and the molar ratio

1. Water/AOT/cyclohexane system

Figure 3 shows that $\epsilon_s=f(\phi)$ is always increasing. The $\epsilon_s=f(n)$ curve goes through a maximum for n close to 5 when ϕ is high (Fig. 4). Figure 5 shows the variations of ν_R as a function of n.

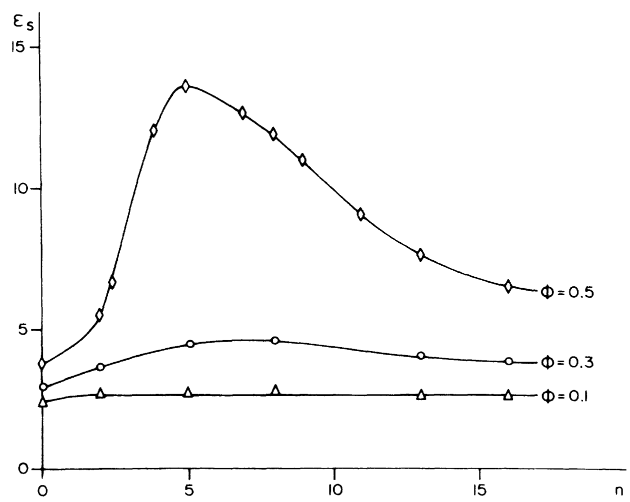

FIG. 4. Water/AOT/cyclohexane system ($T=25\,^{\circ}\mathrm{C}$). Variations of ϵ_s vs n for different values of ϕ.

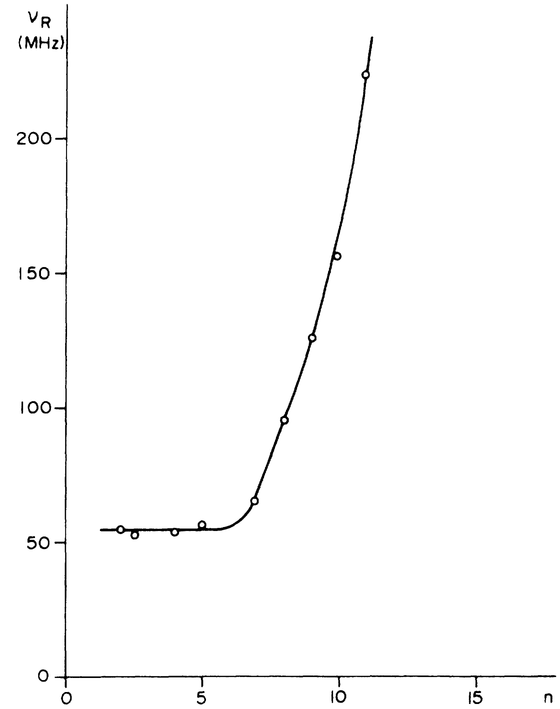

FIG. 5. Water/AOT/cyclohexane system ($\phi=0.50$, $T=25\,^{\circ}\mathrm{C}$). Variations of ν_R (MHz) vs n.

2. Water/AOT/dodecane system (Ref. 5)

Figure 6 represents the $\epsilon_s=f(\phi)$ curves at $n=C^{te}$. If $n\geq 6$ the curves go through a maximum which moves towards small values of ϕ when n increases. Figure 7 shows the variations of ν_R as a function of ϕ at $n=C^{te}$. If $n\geq 6$

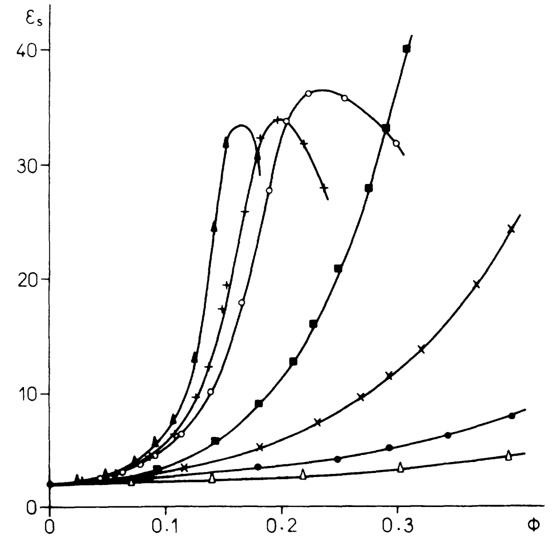

FIG. 6. Water/AOT/dodecane system ($T=25\,^{\circ}\mathrm{C}$). Variations of ϵ_s vs ϕ for different values of n. △, 0; ●, 2; ×, 3.6; ■, 4.4; ○, 6; +, 7; ▲, 10.

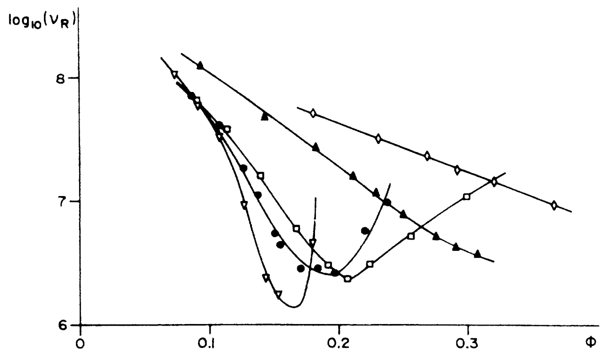

FIG. 7. Water/AOT/dodecane system. Variations of ν_R (Hz) vs ϕ for different values of n. ◇, 3.6; ▲, 4.4; □, 6; ●, 7; ▽, 10.

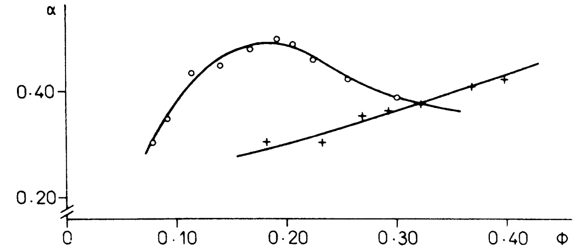

FIG. 8. Water/AOT/dodecane system ($T=25\,^\circ$C). Variations of α vs ϕ. +, $n=3.6$; ○, $n=6.0$.

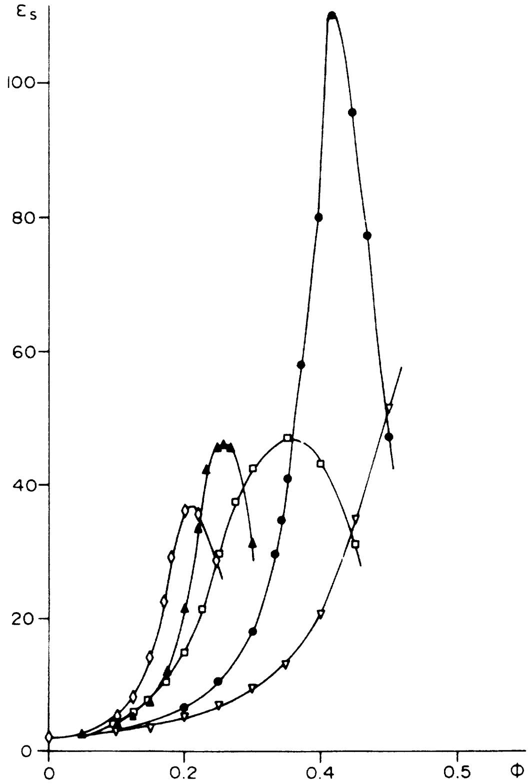

FIG. 9. Water/AOT/undecane system ($T=15\,^\circ$C). Variations of ϵ_s for different values of n. □, 5; ◇, 8; ▲, 11; ●, 18; ▽, 30.

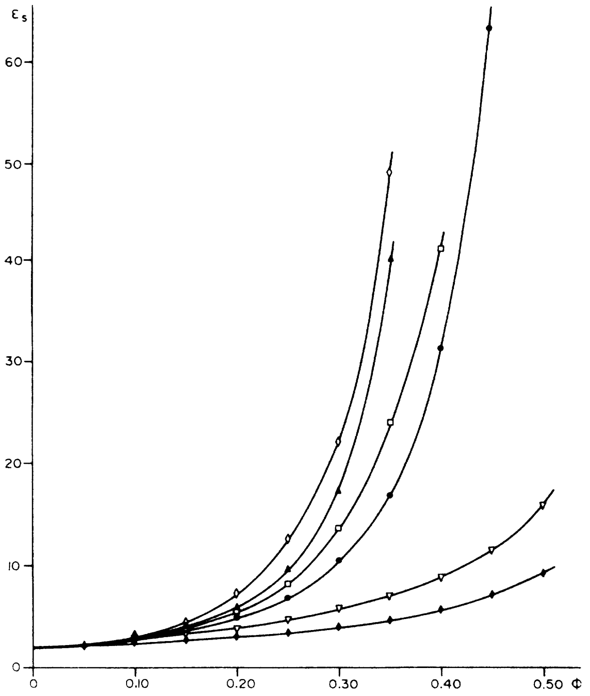

FIG. 10. Water/AOT/iso-octane system ($T=25\,^\circ$C). Variations of ϵ_s vs ϕ for different values of n. ◆, 2; □, 5; ◇, 7; ▲, 10; ●, 13; ▽, 24.

there is a minimum obtained for the same value of ϕ as that corresponding to the maximum of ϵ_s. The variations of α as a function of ϕ are represented in Fig. 8. For $n=6$ the maximum of α corresponds to the maximum of ϵ_s and the minimum of ν_R.

3. *Water/AOT/undecane system*

In order to reduce the conductivity we carried out measurements at 15 °C. Even at that temperature we were only able to measure the static permittivity ϵ_s. The curves obtained are similar to those for dodecane (Fig. 9).

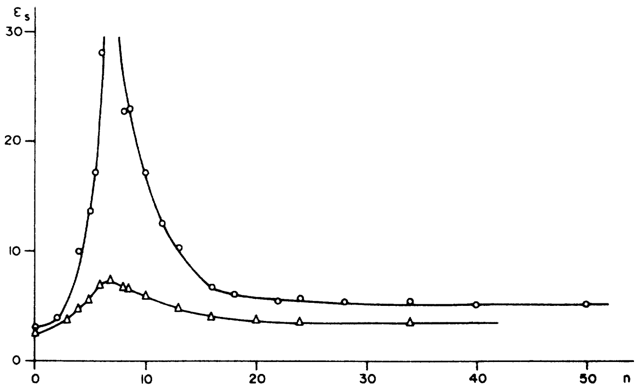

FIG. 11. Water/AOT/iso-octane system (○: $\phi=0.3$, $T=25\,^\circ$C; △: $\phi=0.2$, $T=25\,^\circ$C. Variations of ϵ_s vs n.

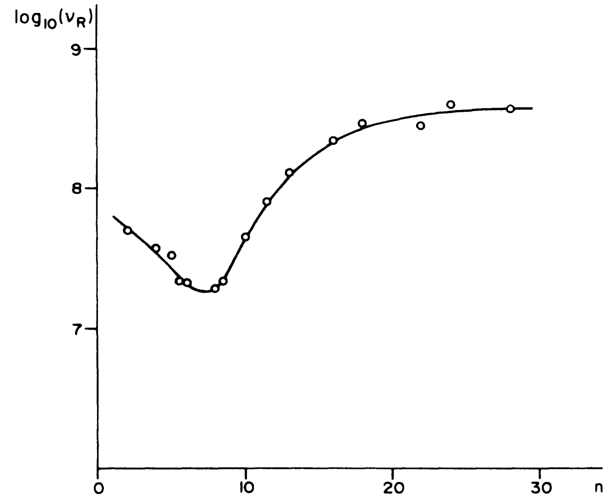

FIG. 12. Water/AOT/iso-octane system ($\phi=0.3$, $T=25\,^{\circ}\mathrm{C}$). Variations of ν_R (Hz) vs n.

4. *Water/AOT/iso-octane system*

Figure 10 represents the variations of ϵ_s as a function of ϕ for various values of n. Figures 11–13 represent for $\phi=0.30$ the variations of ϵ_s, ν_R, and α as a function of n. Figure 14 represents the variations of ϵ_s as a function of n for $\phi=0.2$.

$$\epsilon_s=f(n) \text{ for } \phi=0.2 \ .$$

C. Influence of salt content

This investigation was carried out for the water (+NaCl)/AOT/iso-octane system (Fig. 15). We completed it with the results obtained previously[5] for the water (+NaCl)/AOT/dodecane system.

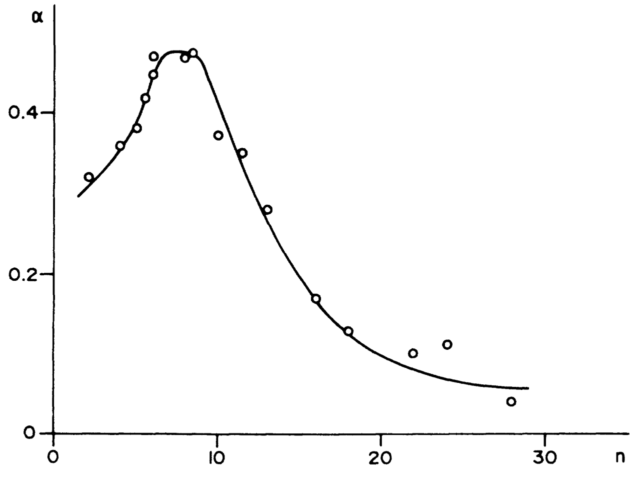

FIG. 13. Water/AOT/iso-octane system ($\phi=0.3$, $T=25\,^{\circ}\mathrm{C}$). Variations of α vs n.

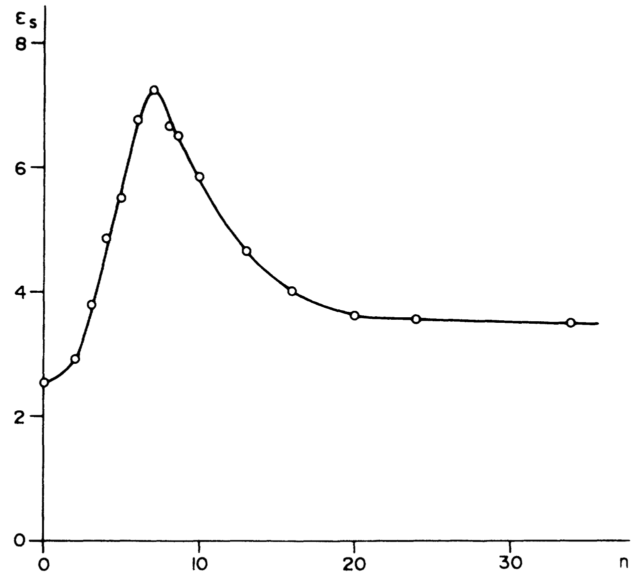

FIG. 14. Water/AOT/iso-octane system ($\phi=0.2$, $T=25\,^{\circ}\mathrm{C}$). Variations of ϵ_s vs n.

Figure 15 represents the variations of ϵ_s as a function of ϕ at $n=8$ for three values of salt content p_s (percentage by weight of salt in aqueous solution). It was noted that the maximum of ϵ_s ($p_s=1\%$) corresponds to a max-

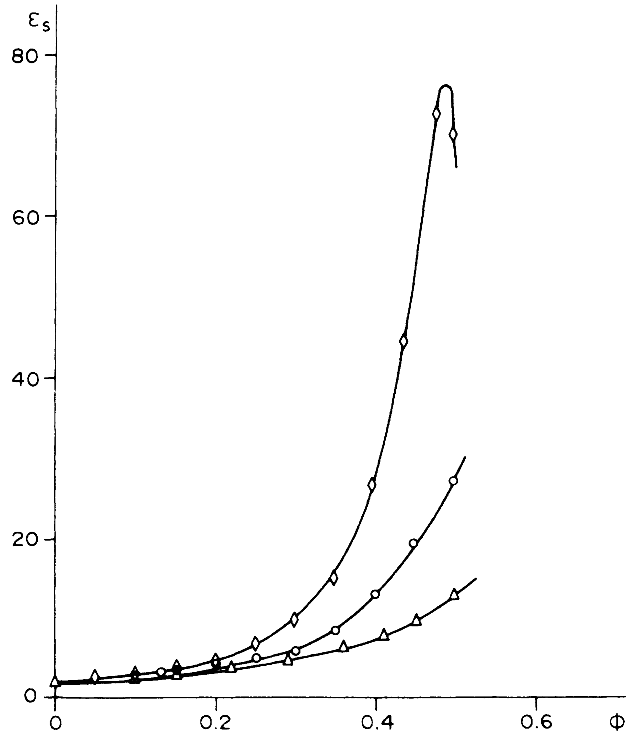

FIG. 15. Water(+NaCl)/AOT/iso-octane system ($n=8$, $T=25\,^{\circ}\mathrm{C}$). Variations of ϵ_s vs ϕ for different values of p_s. ◇, 1%; ○, 2%; △, 3%.

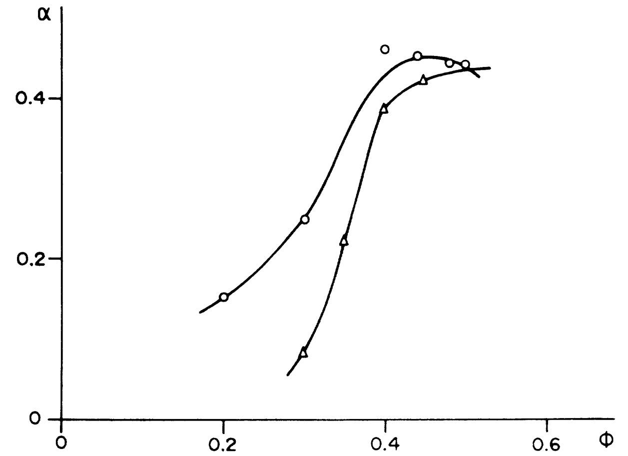

FIG. 16. Water(+NaCl)/AOT/iso-octane system ($n=8$, $T=25\,^{\circ}\mathrm{C}$). Variations of α vs ϕ for different values of p_s. ○, 1%; △, 2%.

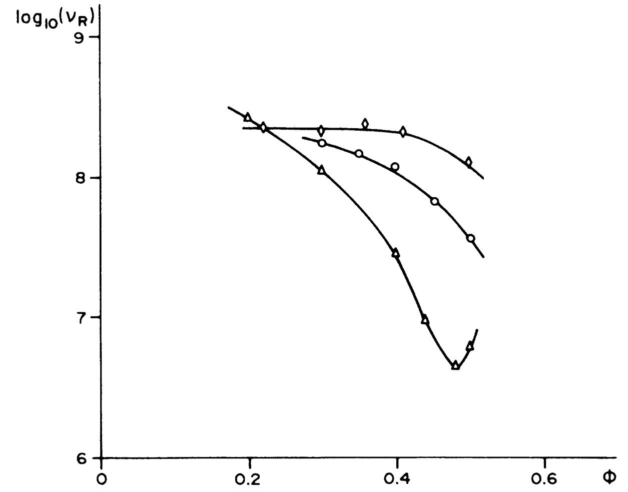

FIG. 17. Water(+NaCl)/AOT/iso-octane system ($n=8$, $T=25\,^{\circ}\mathrm{C}$). Variations of ν_R (Hz) vs ϕ for different values of p_s. △, 1%; ○, 2%; ◇ 3%.

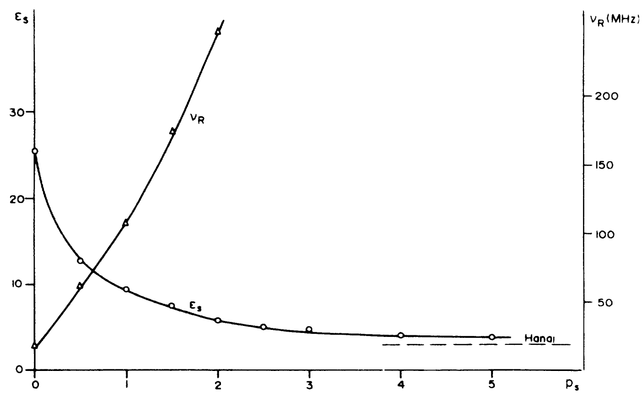

FIG. 18. Water/AOT/iso-octane system ($n=8$, $\phi=0.3$, $T=25\,^{\circ}\mathrm{C}$). Variations of ϵ_s and ν_R (MHz) vs p_s (%).

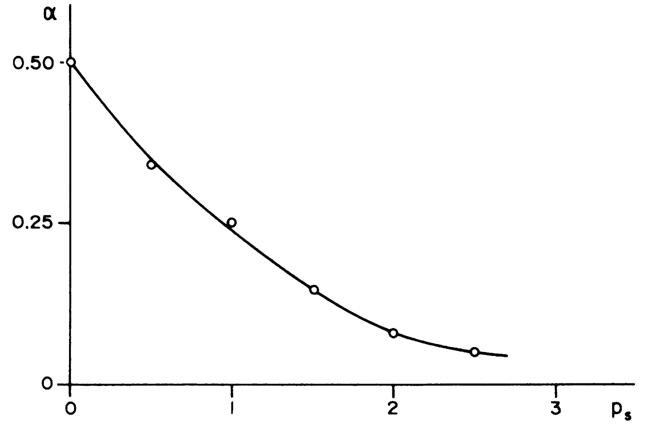

FIG. 19. Water(+NaCl)/AOT/iso-octane system ($n=8$, $\phi=0.3$, $T=25\,^{\circ}\mathrm{C}$). Variations of α vs p_s (%).

imum of α (Fig. 16) and a minimum of ν_R (Fig. 17). Studying the system as a function of p_s at $\phi=0.30$ and $n=8$, we observed that the amplitude of the relaxation and frequency spread α decreases very rapidly when p_s increases, while ν_R increases very rapidly (Figs. 18, 19). We have already reported[5] a similar result for the water (+NaCl)/AOT/dodecane system (Fig. 20).

IV. ANALYSIS OF THE RESULTS

A. Theoretical background

The determination of the complex permittivity of heterogeneous systems is a well-known problem which has attracted many research workers for some time now. From the most general point of view the complex permittivity ϵ^* of a heterogeneous binary system must be accounted for by a relation of the form $\epsilon^*=G(\epsilon_1^*,\epsilon_2^*,\phi,p_k)$ where ϵ_1^* and ϵ_2^* are the complex permittivities of components 1 and 2, ϕ is the volume fraction of constituent 1, and p_k represents parameters which enable the function G to contain all the information on the geometry of the

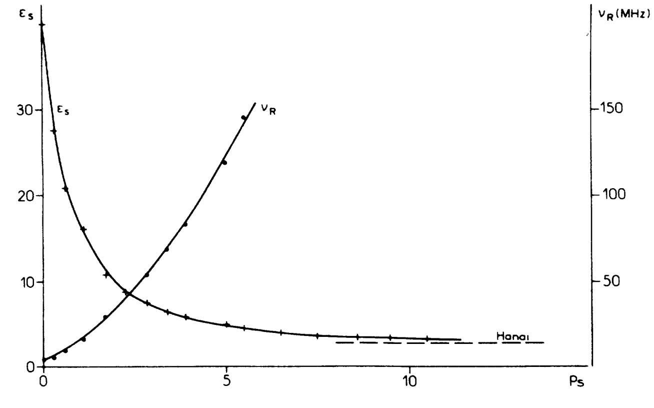

FIG. 20. Water(+NaCl)/AOT/dodecane system ($n=4.4$, $\phi=0.308$, $T=25\,^{\circ}\mathrm{C}$). Variations of ϵ_s and ν_R (MHz) vs p_s (%).

dispersion and on the interactions taking place within the system. The models by which the function G can be obtained are most often based on the effective medium or mean-field theories. They generally yield good results when the interactions in the mixture are weak, which is often the case at low volume fractions of one of the components, and as long as the dispersion can be considered as macroscopically homogeneous. On the other hand, when the dispersed particles can no longer be considered as isolated; in other words, when clusters of varying sizes form, the conventional models no longer apply and the concept or percolation can successfully be used.

We have already indicated in Sec. I that for systems of the water/AOT/oil type, percolation played a part in the description of conductivity. Relations 1 and 2 concerning percolation for conductivity are particular cases of a more general relation concerning complex permittivity:[7,8]

$$\frac{\epsilon^*}{\epsilon_1^*} = |\phi-\phi_c|^{\mu} f\left[\frac{\epsilon_2^*/\epsilon_1^*}{|\phi-\phi_c|^{(\mu+s)}}\right] , \tag{4}$$

where the exponents μ and s are identical to those involved in Eqs. (1) and (2). The function $f(z)$ where z is a complex variable satisfies the following asymptotic forms:

$$\phi>\phi_c, \quad |z| \ll 1, \quad f(z)=c_1+c_1'z ,$$

$$\phi<\phi_c, \quad |z| \ll 1, \quad f(z)=c_2z ,$$

$$|z| \gg 1, \quad \forall\phi, \quad f(z)=cz^{\mu/(\mu+s)} .$$

If one assumes that the two constituents are dielectric conductors of permittivity ϵ_{1s} and ϵ_{2s} and of conductivity σ_1 and σ_2, we have

$$\epsilon_1^*=\epsilon_{1s}-j\frac{\sigma_2}{\epsilon_0\omega}, \quad \epsilon_2^*=\epsilon_{2s}-j\frac{\sigma_2}{\epsilon_0\omega} .$$

The system presents a real permittivity ϵ_s and a conductivity σ. We will determine these two quantities for the following particular cases.

(a) For $\phi<\phi_c$, $|z| \ll 1$ we obtain

$$\epsilon_s=c_2\epsilon_{2s}(\phi_c-\phi)^{-s}, \quad \sigma=c_2\sigma_2(\phi_c-\phi)^{-s} .$$

(b) For $\phi>\phi_c$, $|z| \ll 1$ we obtain

$$\epsilon_s=c_1'\epsilon_{2s}(\phi-\phi_c)^{-s}\left[1+\frac{c_1}{c_1'}\frac{\epsilon_{1s}}{\epsilon_{2s}}(\phi-\phi_c)^{(\mu+s)}\right] ,$$

$$\sigma=c_1\sigma_1(\phi-\phi_c)^{\mu}\left[1+\frac{c_1'}{c_1}\frac{\sigma_2}{\sigma_1}(\phi-\phi_c)^{-(\mu+s)}\right] .$$

As $\mu+s$ is positive and $\epsilon_{1s}/\epsilon_{2s}$ does not go to infinity, when ϕ is close to ϕ_c we obtain

$$\epsilon_s=c_1'\epsilon_{2s}(\phi-\phi_c)^{-s} .$$

Thus, when close to ϕ_c, ϵ_s varies according to $|\phi-\phi_c|^{-s}$ to either side of ϕ_c. Moreover, if $\sigma_2/\sigma_1 \ll 1$ (for example, with a perfect insulator $\sigma_2=0$), close to the percolation threshold one can still find

$$x=\frac{\sigma_2/\sigma_1}{|\phi-\phi_c|^{(\mu+s)}} \ll 1 ,$$

then

$$\sigma=c_1\sigma_1(\phi-\phi_c)^{\mu} .$$

(c) For $|z| \gg 1$, we obtain

$$\epsilon^*=c\epsilon_1^{*[s/(\mu+s)]}\epsilon_2^{*[\mu/(\mu+s)]}$$

and in these conditions ϵ^* is independent of ϕ. Let us assume that the constituent 2 is a perfect insulator ($\sigma_2=0$). If ω is such that $\epsilon_{1s}^2 \ll \sigma_1^2/(\epsilon_0^2\omega^2)$ we obtain

$$\epsilon^* \propto (j\omega)^{-s/(\mu+s)} . \tag{5}$$

When $\phi=\phi_c$ we are still in a situation in which $|z| \gg 1$, whatever the value of ω. Finally, following a suggestion made by Bergman, the following was proposed[9,10] for the relaxation frequency:

$$\nu_R \propto |\phi-\phi_c|^{(\mu+s)} ,$$

valid only when ϕ is near ϕ_c.

B. Dielectric percolation in microemulsions

1. *Threshold of dielectric percolation*

The above relations show that if $\phi \rightarrow \phi_c$, $\epsilon_s \propto |\phi-\phi_c|^{-s}$. This relation is not valid for $\phi=\phi_c(|z| \gg 1)$, and in fact the curve $\epsilon_s=f(\phi)$ must go through a maximum for $\phi=\phi_c$ which can be observed in Figs. 6, 9, and 15. We will use ϕ_{cd} to refer to the value of the percolation threshold determined from the $\epsilon_s=f(\phi)$ curves at $n=C^{te}$. In Fig. 21 we have represented the variations of ϕ_{cd} as a function of n for the

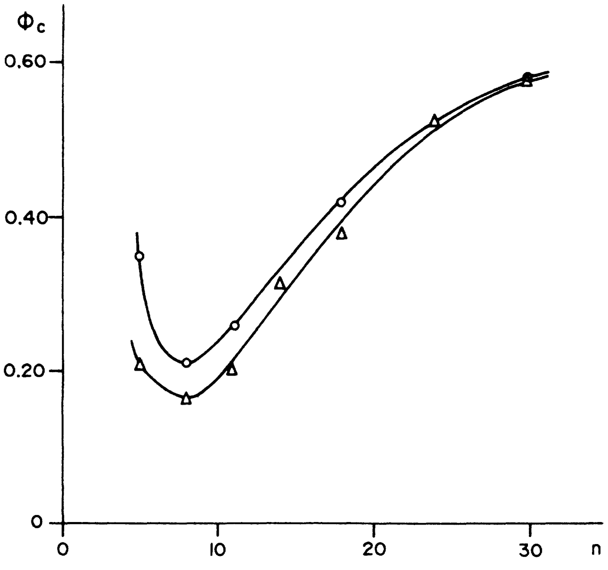

FIG. 21. Water/AOT/undecane system ($T=15$ °C). Variations of the percolation threshold vs n. ○, values for ϕ_{cd} determined with static permittivity; △, values for ϕ_{cc} determined with conductivity.

water/AOT/undecane system at 15 °C. In the same figure we have plotted the $\phi_{cc}=f(n)$ curve which was obtained from the conductivity curves for the same samples. As indicated in a previous paper[1] the values of ϕ_{cc} have been determined by numerical analysis of the data, using Eqs. (1) and (2). We have checked[1] that the values of ϕ_{cc} obtained in that way do fit with the maximum of $d(\log_{10}\sigma)/d\phi$ versus ϕ. It is apparent that the two curves $\phi_{cc}=f(n)$ and $\phi_{cd}=f(n)$ have the same shape and both present a minimum at approximately $n=8$. But the values of ϕ_{cd} are for constant values of n higher than those of ϕ_{cc}. We have reported in Fig. 22 the variations of $d(\log_{10}\sigma)/d\phi$ and ϵ_s as a function of ϕ for the water/AOT/undecane system at $T=15$ °C and $n=8$ (which correspond to Fig. 1 of Ref. 1). One may observe that the locations of the maxima corresponding to ϕ_{cc} and ϕ_{cd} values are quite different. The curves $\phi_{cc}=f(n)$ and $\phi_{cd}=f(n)$ seem to merge together at high values of n. An identical result is obtained for the water/AOT/dodecane system. We should point out that the difference between ϕ_{cd} and ϕ_{cc} has already been observed by Van Dijk[11] for the water/AOT/iso-octane system.

2. *Determination of the critical exponent s*

When $\log_{10}\epsilon_s=f(\log_{10}|\phi-\phi_{cd}|)$ is plotted a straight line of slope s should be obtained close to the threshold. For example, Fig. 23 corresponds to the water/AOT/dodecane system ($n=7$, $T=25$ °C, $\phi_{cd}=0.20$). It is apparent that on this curve no area of linear variation immediately around ϕ_{cd} can be identified. The curve $\epsilon_s=f(\phi)$ goes through a maximum and the slope tends towards zero if $\phi\to\phi_{cd}$. However, there is a linear part if $\phi\leq 0.15$, with a slope of $-\bar{s}$ with $\bar{s}=1.65$. This value does not correspond to the value predicted by the percolation theories ($s=0.7$ for static percolation and $\bar{s}=1.2$ for dynamic percolation). The difference with $\bar{s}$ (value obtained by conductivity) resides no doubt in the fact that we determine the slope relatively far from the threshold and that the development of the function $f(z)$ is only valid if ϕ is fairly close to ϕ_{cd}. It should be pointed out that since ϵ_s does not change by very much, the actual scaling regime may be quite small. We observed that $\bar{s}$ is fairly constant.

If we now allow that the exponent relatively far from ϕ_{cd} is given by $\bar{s}=1.65$, the percolation threshold can be determined in cases where the maximum of curve $\epsilon_s=f(\phi)$ has not been obtained experimentally. To do this, $\epsilon_s^{-1/1.65}$ is plotted as a function of ϕ. Figure 24 shows an example for the water (+NaCl)/AOT/iso-octane system. By this method we were able to complete the $\phi_{cd}(n)$ curve for the undecane (point $n=30$ of Fig. 21) and to plot the $\phi_{cd}=f(n)$ curve for the water/AOT/iso-octane system (Fig. 25). Once again it can be observed that ϕ_{cd} is higher than ϕ_{cc} but that the minimum of the two quantities corresponds to the same value of n. Similarly, Fig. 26 represents the variations of ϕ_{cd} as a function of the salt content for the water (+NaCl)/AOT/iso-octane system.

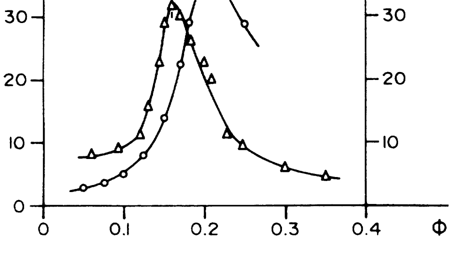

FIG. 22. Water/AOT/undecane system ($n=8$, $T=15$ °C). Variations of ϵ_s (○) and $d(\log_{10}\sigma)/d\phi$(Δ) vs ϕ.

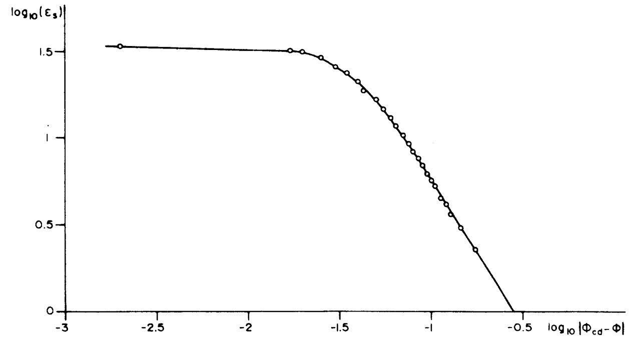

FIG. 23. Water/AOT/dodecane system ($n=7$, $T=25$ °C). Variations of $\log_{10}\epsilon_s$ vs $\log_{10}|\phi_{cd}-\phi|$ ($\phi<\phi_{cd}$).

3. *Behavior of v_R*

We have seen that $v_R\propto|\phi-\phi_c|^{(\mu+s)}$ which indicates that $v_R\to 0$ if $\phi\to\phi_c$ (on either side of ϕ_c). Such behavior is observed experimentally at the maximum of the

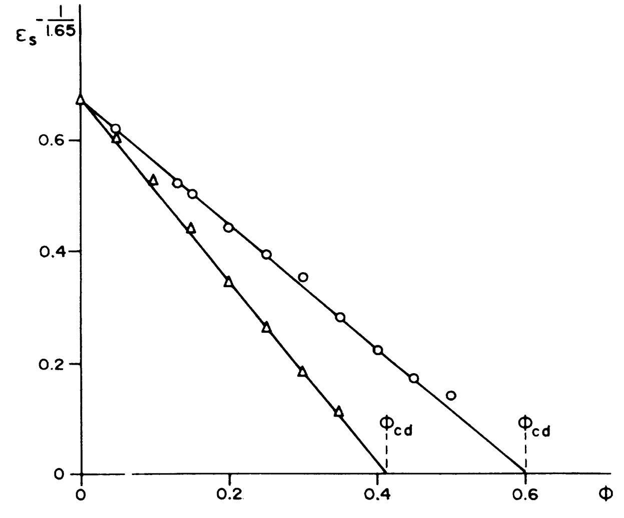

FIG. 24. Water(+NaCl)/AOT/iso-octane system ($T=25$ °C). Variations of $\epsilon_s^{-1/1.65}$ vs ϕ. △, $n=10$, $p_s=0\%$; ○, $n=8$, $p_s=2\%$.

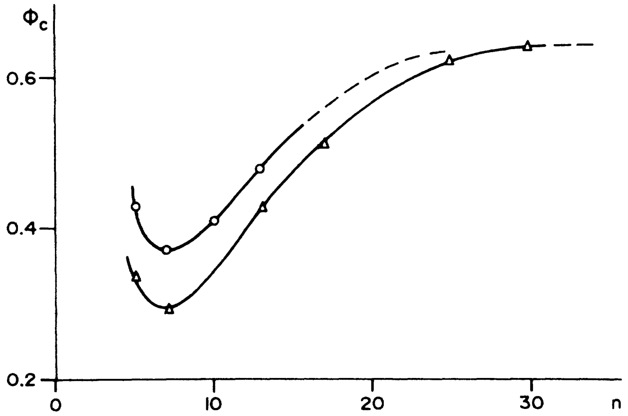

FIG. 25. Water/AOT/iso-octane system ($T=25\,^{\circ}\mathrm{C}$). Variations of the percolation threshold vs n. ○, values for ϕ_{cd} determined with static permittivity; △, values for ϕ_{cc} determined with conductivity.

$\epsilon_s=f(\phi)$ curves, $(\phi=\phi_{cd})$, ν_R is at its minimum. Figure 27 represents the curves of variations of $\log_{10}\nu_R$ as a function of $\log_{10}|\phi_{cd}-\phi|$ for the water/AOT/ dodecane system ($n=7$). In Table I we have reported the values of the slope p which can be compared with the value $\mu+\bar{s}=3.14$. Here one can recall the remarks made by Benguigui. On a metal-insulator system[9] studied in two and three dimensions, he notes that while the scaling theory functions perfectly in two dimensions, differences appear in three dimensions. In particular, the exponent p of the relaxation frequency ν_R is different from $\mu+s$ (in this example it was a case of static percolation), though it remains close (2±0.2 instead of 2.65). He concludes his paper, by saying that the origin of the differences is unclear. However, for the dielectric properties of a peroxide cross-linked polyethylene carbon black composite system,[10] he finds $p=2.6\pm0.2$, agreeing closely with $\mu+s=2.65$ for static percolation. Our results seem therefore to indicate that the relation $\nu_R \alpha |\phi-\phi_c|^{(\mu+\bar{s})}$ is also valid in the case of dynamic percolation, with $\bar{s}=1.2$. This result confirms the suggestion made by Bergman.

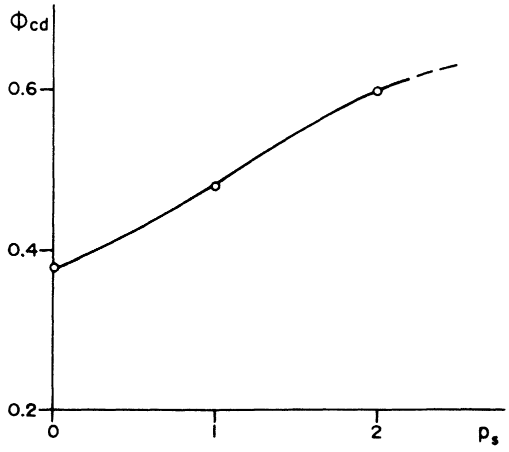

FIG. 26. Water(+NaCl)/AOT/iso-octane system ($n=8$, $T=25\,^{\circ}\mathrm{C}$). Variations of ϕ_{cd} with salt content.

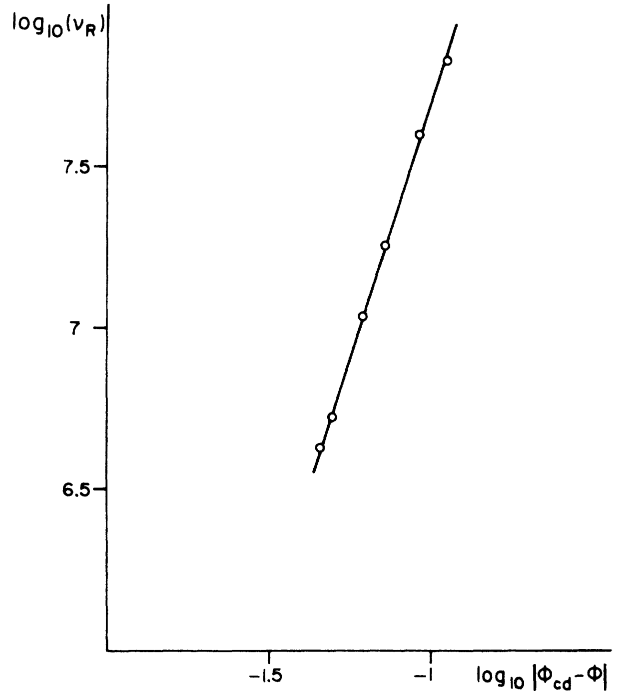

FIG. 27. Water/AOT/dodecane system ($n=7$, $T=25\,^{\circ}\mathrm{C}$, $\phi_{cd}=0.2$). Variations of $\log_{10}\nu_R$ (Hz) vs $\log_{10}|\phi_{cd}-\phi|$.

4. *Variations of ϵ^* at high frequencies*

Equation (3) gives $\epsilon_h^*-\epsilon_h \propto (j\omega)^{-(1-\alpha)}$ if ν/ν_R is high enough. Close to the threshold $|\epsilon_R^*| \gg \epsilon_h$ and as a first approximation we have $\epsilon_R^* \propto (j\omega)^{-(1-\alpha)}$. Close to the threshold, by comparison with Eq. (5), we have $\alpha\rightarrow\mu/(\mu+s)$ if $\phi\rightarrow\phi_{cd}$. If $s=\bar{s}$ we obtain $\alpha\rightarrow 0.54$. Experimentally it is quite clear that α is at a maximum close to the threshold, and has a value of between 0.46 and 0.50. For the water/AOT/iso-octane system, Van Dijk *et al.*[11,12] find $\alpha=0.62$, agreeing closely with $\alpha\rightarrow\mu/(\mu+s)$ if one takes $s=\bar{s}=1.2$.

5. *Results obtained at variable molar ratios*

Measurements carried out at n variable and ϕ constants (Figs. 4, 5, and 11–14) present maxima or minima according to the conditions. As for conductivity[1] the shape of the different quantities $\epsilon_s, \nu_R, \alpha$ as a function of

TABLE I. Water/AOT/dodecane system ($T=25\,^{\circ}\mathrm{C}$). Values of ϕ_{cd} and of the slope p versus n.

n	ϕ_{cd}	p
6	0.23	3.08
7	0.20	3.16
10	0.17	3.09

n can be explained by considering the variations of $|\phi-\phi_{cd}(n)|$. Figure 28 ($\phi=0.3$) is characteristic, and shows clearly that the maximum observed on the $\epsilon_s(n)$ curve is linked to the fact that the quantity $|\phi_{cd}(n)-\phi|$ is then minimal. It can also be noted that when $\phi=0.2$ the maximum of ϵ_s is less marked since $|0.2-\phi_{cd}(n)|^{-s} < |0.3-\phi_{cd}(n)|^{-s}$ (Figs. 11 and 14). The same considerations explain why $\nu_R(n)$ is at a minimum there. Furthermore, on approaching the percolation threshold $\alpha\to\mu/(\mu+\bar{s})$, which allows an understanding of the maximum of the $\alpha(n)$ curve.

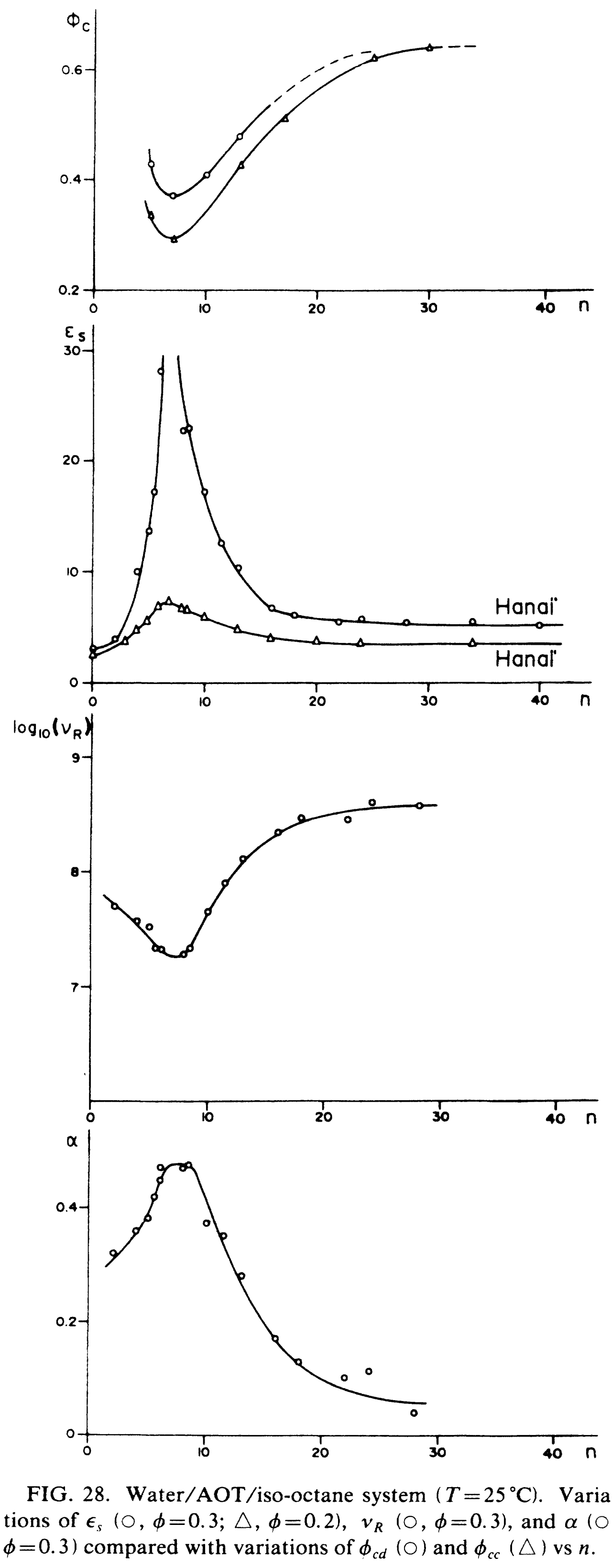

FIG. 28. Water/AOT/iso-octane system ($T=25\,^{\circ}\mathrm{C}$). Variations of ϵ_s (○, $\phi=0.3$; △, $\phi=0.2$), ν_R (○, $\phi=0.3$), and α (○, $\phi=0.3$) compared with variations of ϕ_{cd} (○) and ϕ_{cc} (△) vs n.

Consequently, all these results can be given a highly satisfactory qualitative interpretation within the theory of percolation. As for the quantitative interpretation, it is quite acceptable.

C. Behavior far from the percolation threshold

Before the notion of dielectric percolation was introduced for microemulsions,[11] many authors tried to explain the variations of static permittivity in terms of the conventional mixture laws. They all came up against the problem of the large values of ϵ_s which are encountered close to the percolation threshold. In the context of a spherical dispersion model the maximum value of ϵ_s that can be obtained, for example, by means of Hanaï's law,[13] is given by $\epsilon_s=\epsilon_{2s}/(1-\phi)^3$ (obtained when $|\epsilon_1^*| \gg |\epsilon_2^*|$). If, for example, we take $\phi=0.26$ and $\epsilon_{2s}\simeq 2$ (static permittivity of pure oil) we obtain $\epsilon_s=4.9$. For the same volume fraction, Fig. 9 shows that with the undecane ($T=15\,^{\circ}\mathrm{C}$ and $n=11$), the value measured is equal to 46. Two different approaches have been used in an attempt to explain this difference.

(a) Introduction of an apparent volume fraction:[14] this leads to results that are difficult to accept. In the previous example $\phi_a=0.65$.

(b) Introduction of anisotropic objects:[5,15-17] other authors have reported that spherical particles might aggregate to form clusters, which from the dielectric point of view could be assimilated with revolution ellipsoids. In the case of the water/AOT/dodecane system the analysis (by extension of Hanaï's law to nonspherical cases) yields a high axial ratio, of the order of 9, at the maximum of ϵ_s. Furthermore, the ratio is then itself at a maximum. No other method has been able to confirm anisotropy.

The nature of the phenomenon which leads to the appearance of a maximum of ϵ_s and a minimum of ν_R is now known. However, when the system is far from the percolation threshold one can expect the conventional theories to apply. We have already made such an observation[5] for the water/AOT/dodecane system: one could possibly suggest the involvement of the superficial distribution of charges at the oil/AOT/interface. Figures 18 and 20 show that at very high values of p_s, Hanaï's law yields an acceptable value. Similarly, Figs. 28, 29, and 30 are characteristic. It can clearly be seen (Fig. 30) that if one approaches ϕ_{cd} the experimental points move away from the curve plotted by means of the classical mixture laws, Hanaï's and Maxwell's relations, and Schwarz's theory[18] to account for the superficial charge.

D. Influence of temperature

We did not investigate dielectric properties as a function of temperature. However, a recent paper by Van

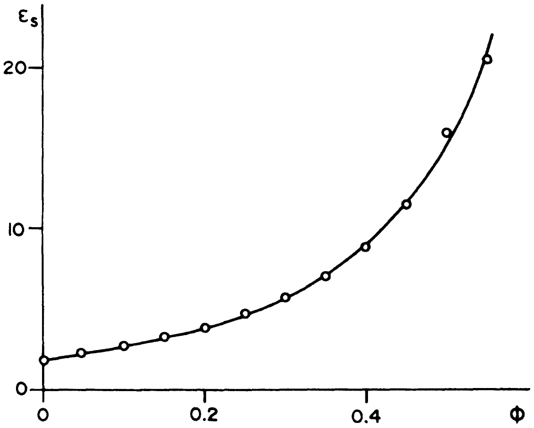

FIG. 29. Water/AOT/iso-octane system ($T=25\,^\circ\mathrm{C}$, $n=24$). Variations of ϵ_s vs ϕ. ○, experimental data; —, curve calculated using the relation $\epsilon_s=\epsilon_{2s}/(1-\phi)^3$ ($\epsilon_{2s}=1.926$).

Dijk *et al.*[12] gives a few indications. They studied variations of static permittivity as a function of temperature for the water/AOT/iso-octane system at $n=27$ for different values of water content, and therefore of ϕ. At constant n and ϕ the static permittivity passes through a maximum at a temperature which decreases as ϕ increases. This result can be interpreted with reference to the theory of percolation by introducing a critical temperature, as has already been done for conductivity.[1] At $T=15\,^\circ\mathrm{C}$ let us consider point B in Fig. 1(a). It is located below the threshold line (NC zone). However, at 25 °C it is located above the threshold (C zone). At a temperature T_c between 15 and 25 °C point B will be located on a threshold line. Therefore, a percolation transition can be observed at constant volume fraction and molar ratio when temperature varies. Furthermore, Fig. 1(a) clearly shows that at constant n, T_c decreases as ϕ increases. It is highly likely that the threshold line ϕ_{cd} undergoes deformation like the threshold line ϕ_{cc} and it will subsequently be apparent that the curve $\epsilon_s(T)$ presents on the one hand a maximum, and on the other hand, that at constant n the maximum is located at a temperature which decreases as the water content rises.

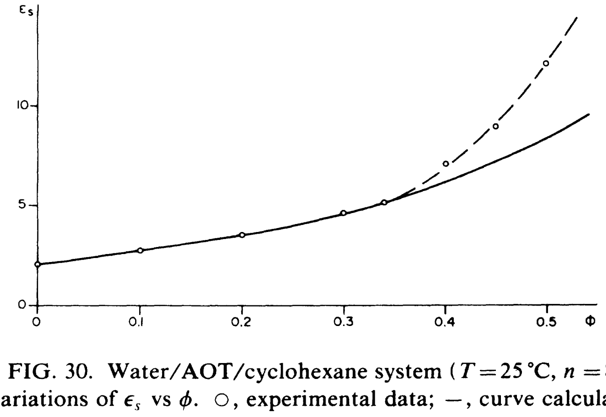

FIG. 30. Water/AOT/cyclohexane system ($T=25\,^\circ\mathrm{C}$, $n=8$). Variations of ϵ_s vs ϕ. ○, experimental data; —, curve calculated using Maxwell's, Schwarz's and Hanaï's relations.

The same variation shape was also observed for the water/AOT/decane system[19] at $n=40.8$. Similarly, it can be predicted that the frequency $\nu_R(T)$ will move through a minimum, corresponding to the maximum of ϵ_s. We observed this behavior in a previous study[20] for quaternary type water/hexadecane/potassium oleate/hexanol microemulsions. But at that time we had no explanation for this unusual result.

V. DISCUSSION

In the course of this study[6] we have shown that experimental results related to complex permittivity of water/AOT/oil microemulsions are conditioned by the phenomenon of percolation, in the same way as results related to conductivity. The existence of a maximum on $\epsilon_s=f(\phi)$ curves does not enable the determination of the theoretical exponent which can only be obtained in the immediate vicinity of the percolation threshold. Our results lead to a value of the exponent far below the threshold equal to $\bar{s}=1.65$, which is slightly higher than the predicted value of $\bar{s}=1.2$. The difference with $\bar{s}$ is undoubtedly due to the fact that, within these conditions, the development of the function $f(z)$ is invalid. The theory of percolation enables satisfactory interpretation of the variation of $\nu_R(\phi)$ and $\alpha(\phi)$. Knowing the $\phi_{cd}(n)$ curves can also allow us to understand the shape of the various curves of $\epsilon_s(n)$, $\nu_R(n)$, and $\alpha(n)$. We also verified that far from the percolation threshold the conventional mixture laws account satisfactorily for the dielectric behavior of the systems studied.

However two problems still remain to be solved: the variations of the value of the percolation threshold, as well as the difference observed between the values of the conductivity threshold ϕ_{cc} and those of the permittivity threshold ϕ_{cd}.

Percolation in ternary water/AOT/oil systems does not seem to be due to the appearance of a bicontinuous structure. For such a structure in the Talmon-Prager model,[21] for example, a single value is obtained for the percolation threshold (≈ 0.15) (Ref. 22) which is in contradiction with our experimental results. Another possibility is to consider the percolation of a binary mixture of hard spheres: in this case the value of ϕ_c is close to 0.15. This value has often been used for microemulsions because it is close to the experimental results obtained under certain conditions for quaternary systems ($\phi_c \approx 0.08$ to 0.14).[23] However, it must be stressed that microemulsions differ from hard-sphere mixtures in several important ways.[24]

(a) The globules have much larger radii than those of oil molecules, and the system cannot therefore be assimilated with a mixture of conducting and nonconducting hard spheres.

(b) A considerable number of experimental or theoretical investigations show that interactions between globules play a fundamental role in the understanding of phase diagrams and light or neutron scattering properties.[25–27] When the interactions increase they bring about demixtion, which occurs as a liquid-gas transition, and there may be a critical point in the phase diagram.[27] In fact, percolation in microemulsions should be treated as the percolation of a dispersion of spheres interacting in a continuous medium. Moreover, the problem should be dealt with in the framework of a dynamic theory[2,28] which is confirmed by the value obtained for the conductivity exponent below the threshold.

In the simple case in which the spheres are identical hard spheres, without interaction, dispersed randomly in an insulating continuous medium, the percolation threshold will be obtained when the spheres come into contact, in other words, at the close-packing volume fraction (≈ 0.65). If there is interaction the threshold varies. Bug *et al.*[29] and Safran *et al.*[24] used numerical analysis to study the variations of ϕ_c with intensity of interactions. This model includes the role of Brownian motion. We will give a brief overview of this model and the essential results it yields.

Interactions between particles of radius $=1$ are modelized by the potential $V(r)$ with

$$V(r)=\begin{cases}\infty & \text{if } r\le 1\\ -U & \text{if } 1<r\le 1+\lambda\\ 0 & \text{if } r>1+\lambda .\end{cases}$$

The intensity of interactions varies with the parameter U which represents the well depth, and the distance of interaction corresponds to the parameter λ.

A shell of thickness δ surrounds each particle, and two particles are considered as belonging to the same cluster if their shells overlap. It should be noted that λ and δ are two independent parameters and that δ characterizes the maximum distance between two spheres for a charge transfer to take place. In this general definition of δ it is not necessary for two spheres to be in contact to belong to the same cluster if it is accepted that they can exchange ions by diffusion through the oil when they are close enough to each other ("hopping"). Also δ can have values higher than the interaction distance λ. If ϕ represents the volume fraction of hard spheres, $\bar{\phi}=\phi(1+\delta)^3$ refers to an effective volume fraction. If $\delta=0$, $\bar{\phi}=\phi$.

Figure 31, based on Ref. 29, represents the variations of $\bar{\phi}_c$ (the value of $\bar{\phi}$ at the percolation threshold) as a function of $1/(1+\delta)$ for $U=0$ and 2.2, λ being fixed at 0.1. One can observe that if $1/(1+\delta)\ge 0.7$, an increase of U, and therefore of the interaction intensity, will reduce the value of the percolation threshold, while the opposite will occur if $1/(1+\delta)<0.7$. If $1/(1+\delta)=1$, i.e., $\delta=0$, the system is made up of hard spheres, and if there are no interactions ($U=0$), the percolation threshold is obtained at 0.65.

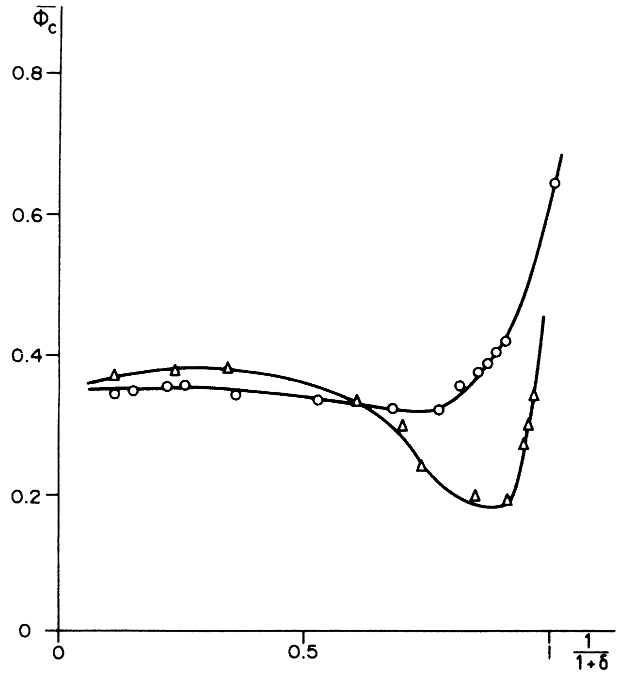

FIG. 31. Curve of variations of $\bar{\phi}_c$ vs $1/(1+\delta)$ (according to Ref. 29). ○, $U=0$; △, $U=2.2$.

The origin for the differences between the conductivity percolation threshold ϕ_{cc} and the permittivity threshold ϕ_{cd} probably lies in the existence of a shell δ reflecting the distance of diffusion of ions between neighboring micelles. As for conductivity, two micelles are considered as belonging to the same cluster if the distance between them is less than $2(1+\delta)$, whereas for permittivity, polarization of the cluster is the important factor, through the intermediary of the constituent with the highest polarity (water), and in this case the droplets must be in contact to be considered as connected. Adopting this hypothesis,

$$\phi_{cc}=\phi_c,\quad \phi_{cd}=\phi_c(1+\delta)^3=\bar{\phi}_c\ .$$

It is therefore possible to estimate the distance of diffusion since $\delta=(\phi_{cd}/\phi_{cc})^{1/3}-1$. From the experimental results one can calculate maximum values of δ of the order of $\frac{1}{10}$, in other words, a few angstroms for the "shell," which is a plausible order of magnitude. Furthermore, when n increases, $\delta(n)$ is observed to fall and tend towards zero (cf. Figs. 21 and 25). It can be emphasized here that the value of the well depth at the critical point corresponds, in a mean-field calculation, to the critical value $U_{\rm cr}$ given by

$$[(1+\lambda)^3-1][\exp(U_{\rm cr})-1]\sim\tfrac{21}{8}\ .$$

If $\lambda=0.1$, we obtain $U_{\rm cr}\sim 2.2$. The theory also provides a critical volume fraction $\phi_{\rm cr}=0.13$. It can be seen in Fig. 31 that the minimum of $\bar{\phi}_c$ obtained when $U=2.2$ (a value very close to $U_{\rm cr}$) corresponds to a value of $\phi_c\sim\phi_{\rm cr}$. In the model proposed by Safran *et al.*, the critical volume fraction $\phi_{\rm cr}$ is a lower limit for the percolation threshold when λ and δ are small. In the case of the water/AOT/decane system, a critical point was identified on the demixtion curve and, according to Honorat *et al.*, $\phi_{\rm cr}=0.127$ at $T_c=25.5\,^{\circ}\mathrm{C}$. It should also be pointed out that in the case of quaternary systems, Cazabat *et al.*[23] show that the critical point is obtained for $\phi_{\rm cr}\sim\phi_c$ for systems in which strong interactions occur. Searching for and determining lines of critical points will probably enhance understanding of the correlations existing between the critical volume fraction $\phi_{\rm cr}$ and the percolation threshold value ϕ_c.

The fact that the value of ϕ_c depends on both U and δ (at fixed λ) shows that any attempt at quantitative interpretation of the variations of the percolation threshold will require knowledge of the interactions occurring in the system. It was possible to draw certain general conclusions from the light scattering measurements. Interactions increase if (a) the ratio n, and therefore the radius of the micelles, increases; (b) the length of the alcohol chain in quaternary systems decreases; (c) salt content decreases; or (d) the nature of the oil changes according to the sequence[23] toluene, cyclohexane, iso-octane, octane, dodecane.

These observations allow a qualitative explanation for a certain number of experimental results. We will assume that charge transfer between droplets can only take place if the globules are sufficiently close together, and therefore if δ is small. Consequently, $1/(1+\delta)$ will be fairly large and in particular >0.7, in agreement with our experimental determinations of $\delta(n)$.

If n is fixed and if salt content is increased, the interactions decrease and it is seen that ϕ_c increases in accordance with Fig. 31. When salt content is high we obtain (Fig. 26) high values of $\phi_c(0.6)$ showing that in this case δ is close to zero and that the droplets behave like hard spheres.

If we plot a curve of the variation of the conductivity percolation threshold (at 25 °C and $n=8$) as a function of the number of carbon atoms C_n of the oil chain, we obtain[6] a decreasing function of C_n consistent with an increase of the interactions (Fig. 32).

The curves of variation[1] of ϕ_{cc} with T can also be explained in the light of the preceding observations. Light scattering measurements[30] show that like U, the distance of interaction λ increases with T. This brings about a reduction in the threshold. It can be observed that at low temperatures the percolation threshold has a high value. If $n=20$, $T=15\,°\mathrm{C}$, we obtain $\phi_{cc}\simeq 0.6$ with the undecane, which shows that U and δ are in that case close to zero. However, at 35 °C, for the same system, we obtain values of ϕ_{cc} close to the critical value ϕ_{cr}, independently of the value of n.

The variations of ϕ_{cc} or ϕ_{cd} with n are more difficult to explain. As the variations of the two thresholds are similar, in the following discussion we will use the notation ϕ_c where ϕ_c will represent ϕ_{cc} or ϕ_{cd} indifferently. For small values of n, ϕ_c is observed to decrease as n increases (Figs. 21 and 25) which is consistent with an increase in interactions with the radius of micelles. When n increases, the interaction U increases, but we have seen that $\delta(n)$ seems to tend towards zero. In these conditions Fig. 31 shows that ϕ_c can increase. This is because the decrease in ϕ_c due to the increase in U can be compensated by the increase in ϕ_c due to the decrease in δ (rising portion of the curve). Finally, it would be interesting to find out to what extent the parameter λ depends on n and therefore influences the value of ϕ_c.

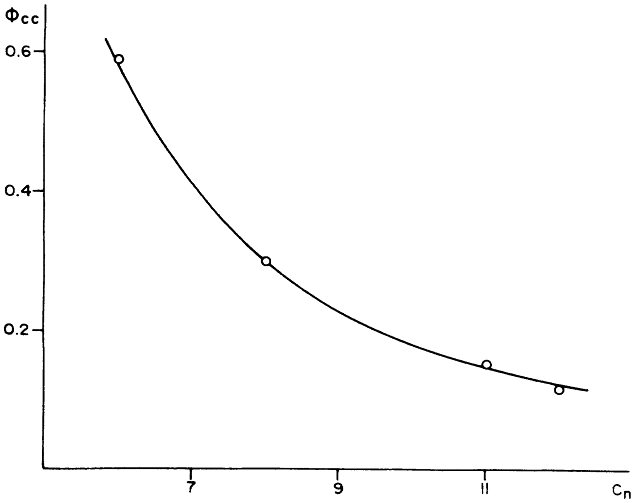

FIG. 32. Variations of ϕ_{cc} vs C_n ($T=25\,°\mathrm{C}$, $n=8$).

Taking the above observations into account, we have a good qualitative and quantitative description of the properties studied for ternary systems of the type, water/AOT/oil. It seems that in certain conditions the same interpretation can be applied to the partial results published on quaternary systems, as we have mentioned. However, the alcohol remains difficult to locate, which makes quantitative discussion impossible.

It is clear on the basis of all the results that for any system (ternary or quaternary, with or without salt, or waterless), considerable prudence is required in the interpretation of "accidents" observed on conductivity, permittivity, dielectric relaxation, viscosity,[6] etc. Before introducing a structural change, one should first verify the nonpercolating character of the system. If the system presents a percolating character, the position of the "accidents" should be studied in relation to the percolation threshold line. If this is not done, there is a risk that false conclusions might be drawn.

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[1] M. Moha-Ouchane, J. Peyrelasse, and C. Boned, Phys. Rev. A **35**, 3027 (1987).

[2] G. S. Grest, I. Webman, S. A. Safran, and A. L. R. Bug, Phys. Rev. A **33**, 2842 (1986).

[3] J. Peyrelasse, C. Boned, and J. P. Le Petit, J. Phys. E **14**, 1002 (1981).

[4] C. Boned and J. Peyrelasse, J. Phys. E **15**, 534 (1982).

[5] J. Peyrelasse and C. Boned, J. Phys. Chem. **89**, 370 (1985).

[6] M. Moha-Ouchane, Thèse de Doctorat, Université de Pau, 1987.

[7] A. L. Efros and B. L. Shklovskii, Phys. Status Solidi B **76**, 475 (1976).

[8] D. Stroud and J. Bergman, Phys. Rev. B **25**, 2061 (1982).

[9] L. Benguigui, J. Phys. (Paris) Lett. **46**, L1015 (1985).

[10] L. Benguigui, J. Yacubowicz, and M. Narkis, J. Polymer Sci. B **25**, 127 (1987).

[11] M. A. Van Dijk, Phys. Rev. Lett. **55**, 1003 (1985).

[12] M. A. Van Dijk, G. Casteleijn, J. G. H. Joosten, and Y. K. Levine, J. Chem. Phys. **85**, 626 (1986).

[13] T. Hanai, Kolloïd Z. u. Z. Polymere **71**, 23 (1960).

[14] R. H. Cole, G. Delbos, P. Winsor, T. K. Bose, and J. M. Moreau, J. Phys. Chem. **89**, 3338 (1985).

[15] J. Sjoblom, B. Jonsson, C. Nylander, and L. Lundstrom, J. Coll. Int. Sci. **100**, 27 (1984).

[16] R. Henze, and U. Schreiber, Ber. Bunsenges. Phys. Chem. **88**, 1075 (1984).

[17] R. Henze, and U. Schreiber, Colloïd Polymer Sci. **263**, 164 (1985).

[18] G. Schwarz, J. Phys. Chem. **66**, 2636 (1962).

[19] S. Bhattacharya, J. P. Stokes, M. W. Kim, and J. S. Huang, Phys. Rev. Lett. **55**, 1884 (1985).

[20] J. Peyrelasse, V. E. R. McClean, C. Boned, R. J. Sheppard, and M. Clausse, J. Phys. D **11**, L117 (1978).

[21] Y. Talmon, and S. Prager, J. Chem. Phys. **69**, 2984 (1978).

[22] G. R. Jerauld, L. E. Scriven, and H. T. Davis, J. Phys. C **17**, 3429 (1984).

[23] A. M. Cazabat, D. Chatenay, D. Langevin, and J. Meunier, Far. Discuss. Chem. Soc. **76**, 291 (1982).

[24] S. A. Safran, I. Webman, and G. S. Grest, Phys. Rev. A **32**, 506 (1985).

[25] A. M. Cazabat, D. Chatenay, D. Langevin, and A. Pouchelon, J. Phys. (Paris) Lett. **41**, L441 (1980).

[26] S. H. Chen, Physica **137B**, 183 (1986).

[27] D. Roux, A. M. Bellocq, and M. S. Leblanc, J. Chem. Phys. Lett. **94**, 156 (1983).

[28] M. Lagues, J. Phys. (Paris) Lett. **40**, L331 (1979).

[29] A. L. R. Bug, S. A. Safran, G. S. Grest, and I. Webman, Phys. Rev. Lett. **55**, 1896 (1985).

[30] P. Honorat, D. Roux, and A. M. Bellocq, J. Phys. (Paris) Lett. **45**, L961 (1984).