Dielectric Study of Percolation Phenomena in a Microemulsion

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The complex permittivity of a three-component water-in-oil microemulsion was measured as a function of frequency, temperature, and volume fractions. A conductivity threshold, associated with a permittivity maximum, was observed and is explained in terms of percolation theory. The experimental value of the critical exponent of the frequency dependence of the permittivity, $u = 0.62 \pm 0.02$, is in good agreement with theoretical predictions.

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There is currently a growing interest in the properties of percolating systems.[1,2] Most studies have dealt with the theoretical aspects and computer simulations of the systems, but there have been relatively few reports of experimental systems exhibiting such effects. As the percolation phenomenon is essentially a connectivity effect, it is expected to be manifested most markedly in transport properties. Indeed, most computer experiments have dealt with the conductivity of random resistor networks.[3-5] However, the complex dielectric permittivity $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) - i\kappa/\omega\epsilon_v$, where κ is the dc conductivity and ϵ_v is the vacuum permittivity, can also be calculated in systems containing both resistive and capacitive bonds. A variety of approaches, including computer simulations,[6,7] analytical methods,[8-10] and effective-medium theory,[11] all predict a divergence of $\epsilon'(\omega = 0)$ at the percolation threshold for the dc conductivity. Here we report the experimental observation of this phenomenon in the three-component microemulsion system of AOT, water, and iso-octane.

A microemulsion is a thermodynamically stable, isotropic, single-phase fluid containing large amounts of two immiscible liquids such as water and hydrocarbon and one or more surface-active agents (surfactants).[12] A surfactant molecule has a polar, hydrophilic head group and an apolar, lipophylic tail. AOT, sodium di-2-ethylhexylsulfosuccinate, is an anionic surfactant molecule with a SO_3^- head group and two hydrocarbon tails. Because of their chemical nature surfactant molecules tend to be localized at the water-oil interface, thereby reducing the surface tension to very small values. A further decrease of the free energy of the system is achieved by contributions from the bending stress[13] and the increase of entropy associated with a fine mixing of the two phases to form a homogeneous microemulsion. In a water-in-oil (W/O) microemulsion such as the one studied here, the water is in the continuous oil phase in the form of small (5–10 nm) spherules surrounded by a monomolecular layer of the surfactant molecules.[14] When the head groups of the surfactant molecules can dissociate in the water phase and donate an ion (e.g., Na^+ in our case), the W/O microemulsion essentially consists of particles with a high conductivity and permittivity immersed in a medium of very low conductivity and permittivity. As the water volume fraction can be large (> 15%), this system may exhibit percolation phenomena. Indeed, a conductivity threshold had previously been observed in multicomponent microemulsions[15-17] and attributed to a percolation transition.

The AOT used in the experiments was obtained from Fluka AG (purum) and inorganic impurities were removed following Tavernier.[18] Iso-octane (2,3,4 trimethyl pentane) was obtained from Baker and the water was deionized and quadruple distilled. The dielectric permittivity measurements were carried out with a Hewlett-Packard HP4917A impedance analyzer (frequency range of 10 kHz–13 MHz) and a Rohde & Schwarz ZPV Vector voltmeter (10 MHz–1 GHz), with use of a thermostated cell.[19] The temperature accuracy was better than 0.1 °C. The dc conductivity was calculated from the observed linear ω dependence of ϵ'' at low frequencies (< 100 kHz). These values were in excellent agreement with the conductivities obtained in experiments using a YSI Model 31 conductivity bridge. The volume fraction of water, δ, was changed by varying the amount of oil and keeping the molar ratio $W_0 = [H_2O]/[AOT]$ constant.[20] The value of δ was calculated by taking the density of AOT to be 1.1 g/ml. All of the mixtures studied here were optically clear within our temperature range and no phase separation could be detected in a period of weeks. The effects reported are therefore different from the phenomena associated with a cloud point.[21]

Figure 1 shows that the AOT–water–iso-octane system exhibits a sharp transition from very low (< 0.1 μmho/cm) to high (> 1000 μmho/cm) conductivity. The transition can be brought about either by an increase of the temperature at a fixed volume fraction δ or by an increase of δ at a fixed temperature. A very interesting feature of the system is that this transition is associated with a pronounced maximum in the low-frequency limit ϵ'_{lf} of the permittivity.

The frequency dependence of ϵ, Fig. 2, shows a dielectric relaxation process for which the ϵ'_{lf} is temperature dependent while the high-frequency limit (just outside the measurement range) appears to be

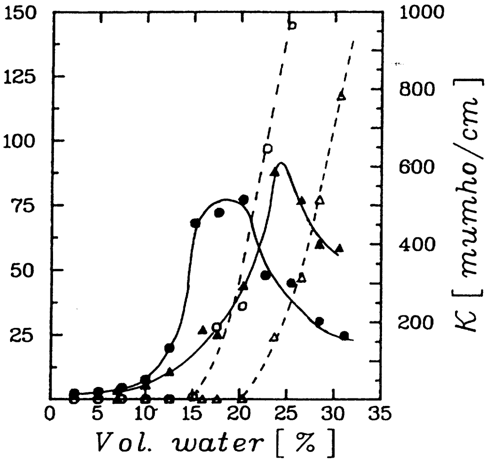

FIG. 1. Low-frequency dielectric permittivity ϵ_{lf}' (closed symbols) and dc conductivity κ (open symbols) vs volume fraction of water of two different samples: $W_0 = 25$, $T = 45\,°\mathrm{C}$ (circles) and $W_0 = 35$, $T = 40\,°\mathrm{C}$ (triangles). The lines serve as a guide to the eye.

essentially independent of temperature. The apparent volume fraction (temperature) of the conductivity threshold is systematically slightly lower than the volume fraction (temperature) at which ϵ_{lf}' reaches its maximum value. This is probably a result of microscopic dynamical phenomena such as the conduction by charged globules. The experimental results at different temperatures show that κ becomes approximately linearly dependent on δ for high values of δ, as predicted by effective-medium theory and computer simulations.[3] The extrapolation of this linear dependence to zero conductivity yields, within experimental error, the volume fraction for which ϵ_{lf}' attains its maximum value. The high but finite values of $\epsilon_{\mathrm{lf}}' \approx 10^2$ can be rationalized in terms of effective-medium theory if the ratio of the particle to bulk conductivities is $\approx 10^5$. The conductivity of the system below the threshold amounts to $\approx 10^{-1}$ μmho/cm, so that we estimate the conductivity of the water phase to be $\approx 10^4$ μmho/cm, which is a quite reasonable value.[22].

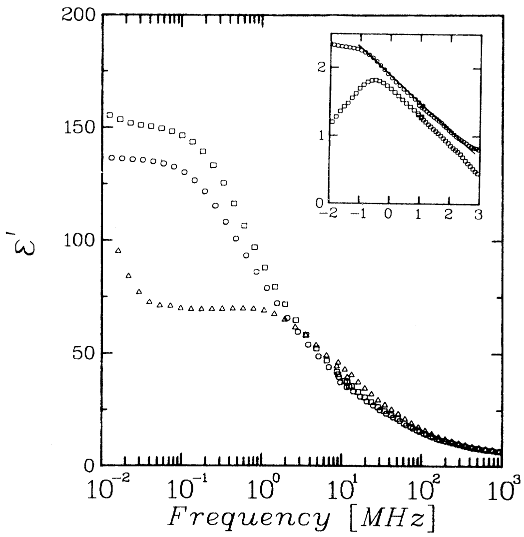

FIG. 2. Frequency dependence of the real part ϵ' of the dielectric permittivity of a solution with $W_0 = 25$ and $\delta = 23.1\%$ at three different temperatures: 38 °C (circles), 39 °C (squares), and 43 °C (triangles). The ϵ_{lf}' attains its maximum at 39 °C. The increase of ϵ' at frequencies below 100 kHz is due to electrode polarization. The inset shows a log-log plot of ϵ' (circles) and ϵ'' (squares) vs frequency of a different solution ($W_0 = 35$, $\delta = 20.3\%$, $T = 42\,°\mathrm{C}$). The straight line segment indicates $\epsilon' \sim \omega^{-0.40}$ at intermediate frequencies.

The results presented above indicate a percolation effect in the system. This conclusion is strongly supported by considering the loss angle Δ, defined by $\tan[\Delta(\omega)] = \epsilon''(\omega)/\epsilon'(\omega)$. If the "solvent" is perfectly insulating, the permittivity at the percolation threshold δ_c is given by[8,9,23]

$$\epsilon(\omega) = E e^{i(\pi/2)(1-u)} (\omega/\omega_0)^{u-1}, \quad \omega \ll \omega_0, \tag{1}$$

where E is a real-valued prefactor and ω_0 a microscopic frequency scale. From (1) we deduce that the loss angle is independent of frequency at $\delta = \delta_c$:

$$\Delta(\omega \ll \omega_0) = \Delta_c = \tfrac{1}{2}\pi(1-u). \tag{2}$$

Figure 3 shows that Δ is indeed constant over a large frequency interval when the microemulsion is close to its percolation threshold. The deviation at the high-frequency side occurs close to the characteristic fre-

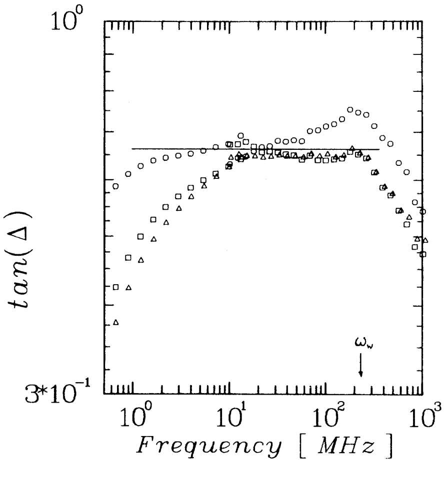

FIG. 3. Log-log plot of the loss angle Δ vs frequency for three different solutions: $W_0 = 35$, $\delta = 34.2\%$, $T = 39\,°\mathrm{C}$ (triangles); $W_0 = 35$, $\delta = 22.4\%$, $T = 40\,°\mathrm{C}$ (squares); and $W_0 = 25$, $\delta = 20.7\%$, $T = 43\,°\mathrm{C}$ (circles). At the given temperatures ϵ_{lf}' attained its maximum value. The arrow marks the characteristic frequency of the water phase ω_w. The horizontal line indicates $\tan\Delta = 0.67$.

quency of the water phase $\omega_w = \kappa_w / \epsilon_w \epsilon_v = 1.4 \times 10^9$ rad/sec. Here we have used $\epsilon_w = 80$ and the observed value $\kappa_w = 10^4$ μmho/cm. The deviation at the low-frequency side is due to the nonzero dc conductivity below the percolation threshold.[8] From Fig. 3 we find $\tan\Delta_c = 0.67 \pm 0.03$. Equation (2) then yields $u = 0.62 \pm 0.02$. According to (1) u can also be obtained from the frequency dependence of $\epsilon(\omega)$. Figure 2 (inset) shows that there is indeed a power-law frequency dependence of ϵ. From this and similar plots we find $u = 0.60 \pm 0.05$ in good accord with the result from (2). The experimentally determined value of u can thus be given as $u = 0.62 \pm 0.02$. This value is in excellent agreement with theoretical values in Ref. 7 (0.65) and Ref. 8 (0.62) and somewhat lower than values in Ref. 4 and Ref. 9 (around 0.75). Unfortunately, the present results do not allow an accurate determination of the critical exponents t and s of conductivity and permittivity.[4] This is mainly due to the fact that the system has a nonzero conductivity below the percolation threshold and the associated uncertainty of δ_c.

It should be understood that a microemulsion is a very complex dynamical system and it cannot be expected that theories based upon simplified static models will provide a quantitatively accurate description. Consequently, the agreement between the predictions of percolation theory and the experimental dielectric properties is striking.

Finally we note that there is a substantial amount of evidence that the basic structure of AOT microemulsions at $W_0 < 60$ is polydispersed spheres of water droplets in a continuum oil medium up to very high dispersed volume fractions[24] as opposed to bicontinuous structures.[25] The present work does not refute either one of these models. If the droplets retain their discrete character, our results indicate a tendency to cluster at high volume fractions and temperatures due to attractive interactions[26,27] with the possibility of charge transfer between droplets which eventually, at sufficiently high temperature and concentration, leads to percolation structures. There are experimental indications from self-diffusion measurements[27,28] that such processes take place.

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