PHYSICAL REVIEW A VOLUME 34, NUMBER 1 JULY 1986

Percolationlike phenomena in oil-continuous microemulsions

Mahn Won Kim and John S. Huang
Exxon Research and Engineering Company, Annandale, New Jersey 08801

(Received 5 March 1986)

We have observed in a three-component oil-continuous microemulsion a new percolation phenomenon. The system of interest consists of anionic surfactant-coated water droplets dispersed in oil. The percolation limit ϕ_p is found to be strongly temperature dependent, while the structure of the microemulsion remains constant. We have proposed a surfactant anion hopping model with a temperature-dependent hopping range. Percolation occurs when the effective droplet volume, as defined by the hopping range, exceeds the hard-sphere close-packing limit of 0.65.

It has now been reasonably well established that for a three-component oil-continuous microemulsion containing water, oil, and AOT [sodium di(2-ethylhexyl)sulfosuccinate] at low to moderate water concentration, the thermodynamically stable clear liquid consists of mainly minute surfactant-coated water droplets of an average size in the range of 30–50 Å depending on the water to AOT ratio.[1-3] It is also known that for volume fraction between 3% and 50% of the dispersed phase (which is the aqueous phase) both the size and the size distribution function of the water droplets remain constant with respect to temperature variations in the temperature range between the 15 °C and the critical point (36 °C). For example, at the critical volume fraction of water and surfactant, (~8%), the droplet size as determined by small-angle neutron scattering remains unchanged to within 10% not only throughout the single phase region, but also in both of the two coexisting microemulsion phases above the critical temperature.[2] In fact, the microemulsions described above have been successfully modeled by a hard-sphere liquid with a short-range square-well attractive interaction,[4] and the basic droplet structure is fairly insensitive to both the concentration of the droplets and the equilibrium temperatures. Thus, it seems to be quite interesting to note that the percolation limit observed in this system is found to be very temperature sensitive. At any given volume fraction of the aqueous phase above 5%, percolation phenomenon has been observed with respect to the temperature, and likewise, at given temperature between 15 and 50 °C, percolation depends on the volume fraction of the aqueous phase.

First, let us describe the dispersed droplet phase in more detail. We know that for an average droplet of 50-Å radius, there are approximately 500 anionic surfactant molecules on the interface. If one-third of the sulfonate groups are ionized, the aqueous phase would contain roughly $0.6M$ monovalent ions, so that the water droplets can be considered as conducting spheres imbedded in a nonconducting decane oil matrix. Furthermore, it is also known that the water droplets are coated with the surfactants whose hydrocarbon tails point outward to the continuous oil phase; and they interact with one another between the droplets with short-range attractive potentials.[4] In this Rapid Communication we shall discuss some conductivity measurements for the microemulsion systems. It is found that our results cannot be analyzed in terms of the conventional percolation theories[5,6] or the stirred percolation theory[7] appropriate for fluids. Recent results of Monte Carlo simulation[8] indicated that a short-ranged interaction potential between the droplets may be sufficient to account for the observed low percolation threshold, provided that a conduction shell with an appropriate thickness around each droplet can be defined so that the effective conducting phase volume reaches the percolation limit. Even though this theory may not explain all the conductivity data obtained in our three-component microemulsions, we believe that it serves as an excellent starting point for our discussion of the observed percolation phenomena.

The procedures for sample preparations are described elsewhere.[2] Conductivity measurements were carried out with a HP-4274A *LCR* meter in a conductivity cell with a cell constant of 1.0 Ω cm^{-1}. Temperature during the measurements was regulated to within 0.1 °C. The concentration of the water phase is known to be better than ± 1%. In Fig. 1 we show temperature dependence of the

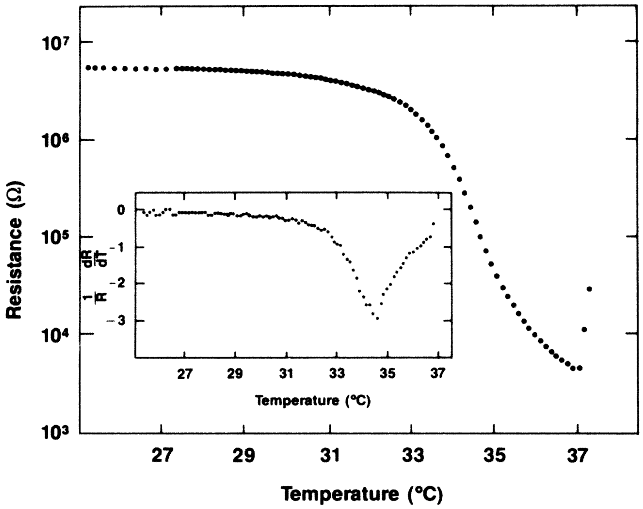

FIG. 1. The temperature dependence of the resistance of three-component microemulsion with $\phi = 0.08$ on a semilog scale. The inset depicts the temperature resistance coefficient $(1/R)dR/dT$ obtained from data displayed in this figure. The inverted cusp defines the percolation temperature T_p.

conductivity of a microemulsion containing 5.0% of water. The inset shows the temperature resistance coefficient $\alpha = (1/R)dR/dT$ exhibiting a sharp peak at 34.6 °C marking the position of the percolation temperature (T_p). It should also be noted that the peak value of α is 200%/°C, approximately two orders of magnitude higher than that of a typical thermistor. Critical temperature of this system is measured to be around 36 °C, roughly 1.5 °C higher than T_p. However, since similar behavior was observed for the same microemulsion at much higher droplet concentrations, far away from the critical point (Fig. 2), we believe that the percolation phenomenon is not related to the critical transition *per se.* The water concentration of the microemulsion in Fig. 2 is 40%, corresponding to the dispersed phase volume (includes the volume of the surfactant) of over 55%. Yet even at this concentration, the system remained nonconducting at low temperatures until 18 °C was reached. Percolation with respect to volume fraction (ϕ_p) of the conducting phase at constant temperature shows the same strong concentration dependence of the percolation limit. Figure 3 shows an apparently normal percolation behavior at 25 °C. The percolation limit as determined by position of the inflection point in the conductivity curve is put at 25%. At higher temperatures, the percolation limit is correspondingly lower. The inset in Fig. 3 displays the temperature dependence of the percolation limits on a log-log scale. A simple power-law fit with a slope of 0.25 is shown.

Percolation phenomena with respect to both the temperature and the volume fraction of the conducting phase can be described by a simple power law at above the percolation limits (Fig. 4). The indices (t) that characterize the power-law divergence for $\phi > \phi_p$, or $T > T_p$ apparently have the same value of 1.7 ± 0.1, while the indices (s) that characterize the power law for $\phi < \phi_p$, or $T < T_p$ are also the same (1.2 ± 0.1). The results described above are found to be independent of the applied voltage of the oscillator below 10 V, and virtually independent of the frequency for frequencies below 100 kHz.

What we have seen in the microemulsion system may be that of percolation phenomenon in a hard-sphere liquid

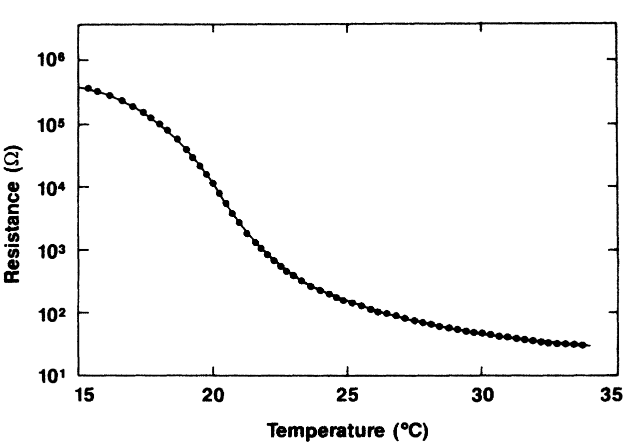

FIG. 2. The percolation behavior of a microemulsion with $\phi = 0.565$. Note that even at this high volume fraction of the conducting phase, the system is nonconducting at 15 °C.

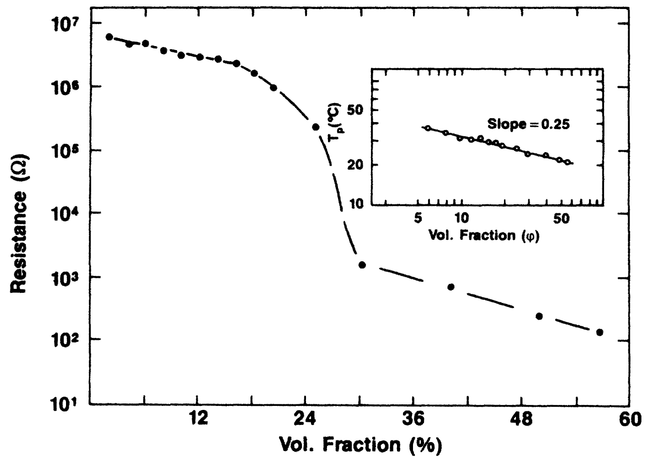

FIG. 3. Percolation behavior observed as a function of the conducting volume fraction observed at $T = 25$ °C. The inset displays the temperature dependence of the percolation limits on a log-log scale.

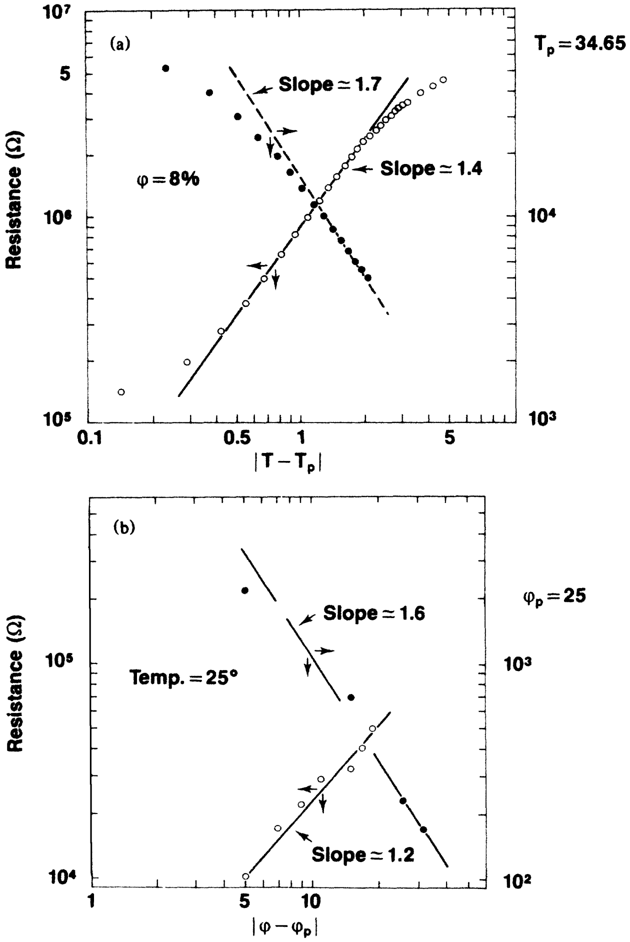

FIG. 4. Scaling behavior of the resistivity at $T = 25$ °C. (a) Scaling with respect to temperature at $\phi = 0.08$. Open circles describe the power-law dependence below T_p: $R \sim |T_p - T|^{1.4}$ and the filled circles describe the power law above T_p: $R \sim (T - T_p)^{-1.7}$. (b) Open circles describe the scaling with respect to $\phi_p - \phi$ below the percolation limit: $R \sim |\phi_p - \phi|^{1.2}$. Filled circles describe the scaling above the percolation limit: $R \sim |\phi - \phi_p|^{-1.6}$.

with attractive interactions. Since each conducting droplet is coated with an insulating layer of the surfactant on the interface, one must assume that the conduction takes place either by the displacement current through the capacitance coupling between the droplets or by hopping of the charged surfactant anions. The absence of the frequency dependence at lower frequencies (100 Hz–100 kHz) over three orders of magnitude does not support the capacitive conduction model. On the other hand, the anion hopping model implies that the formation of charged droplets in a low dielectric medium is allowed. The free energy of forming a charged droplet in oil plus a free anion can be estimated as follows: The radius of the water core is about 50 Å as determined by small-angle neutron scattering (SANS) by Kotlarchyk, Chen, Huang, and Kim.[2] If an AOT surfactant should leave the droplet and leave the counterion (Na^+) in the water core, the static electric energy is of the order of 17 kT. But the total free-energy change must include the entropy gain of the free ion: $\mu_Q = k_B T \ln(f)$, where f is the volume fraction occupied by the anions.[9] Assuming 0.1% of the droplets are charged, μ is found to be of the order of 15 kT. This tends to indicate that it is possible for the surfactant anions to leave the droplets and be reabsorbed onto a second droplet. The time scale needed for the surfactant hopping to occur is of the order of 3×10^{-6} sec, which is the time for an ion to travel 50 Å by diffusion. If this mechanism is correct, frequency-dependent conductivity is expected to occur in the megahertz range, which is indeed being observed by Bhattacharya, Stokes, Kim, and Huang.[10] The temperature dependence of the conductivity can be explained in the following way: Suppose that the surfactant anion has a certain probability to leave the droplet depending on the temperature, and once the anions leave the droplet, they have an effective range of diffusion, δ. If two droplets are within this interaction range, charge transfer is assumed to occur. This range of interaction effectively increases the radius of the droplets. When the effective volume fraction reaches 0.65, the close-peak limit of hard spheres, we must assume that the percolation occurs. The percolation limit T_p depends on the volume fraction of the droplet phase through the following empirical relation between 5 and 56%,

$$T_p \propto \phi^{-0.25} , \qquad (1)$$

where T_p is the percolation temperature measured in the celsius scale. We may then conclude from the relation $(R+\delta)^3/R^3\phi = 0.65$, the temperature dependence for δ,

$$\delta = R(0.018T_p^{4/3} - 1) . \qquad (2)$$

For microemulsions at 25 °C and an average radius of 50 Å, δ is expected to be of the order of 15 Å, a value that seems to be eminently reasonable to us. The sensitivity of the range of interaction to temperature reflects the combined effect of increased probability of the surfactant to be ionized and the increased range of diffusion as the mobility of the ion increases with increasing temperature.

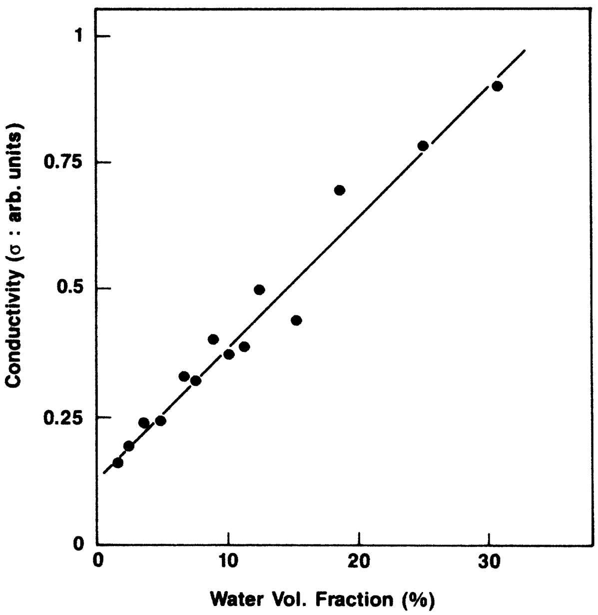

FIG. 5. The conductivity of microemulsion in the plateau region is plotted against the water volume fraction. The linear relationship indicates the fact that the surfactant anions (which are proportional to water concentration) are the charge carriers.

Finally, we have also examined the conductivity (σ) of the microemulsion as a function of the water droplet number density. At temperatures well below the percolation temperature T_p, in the plateau region σ is proportional to the water concentration (Fig. 5). Since the surfactant anion concentration is proportional to the number density of water droplets, this result is consistent with the fact that the surfactant anions are the charge carriers.

There are two other mechanisms which might lead to percolation but are found to be inconsistent with other observations made in this microemulsion system. The first one is the formation of a bicontinuous phase, i.e., both the oil and the water phase form physically continuous paths. This contradicts the small-angle neutron scattering results of Kotlarchyk *et al.*[2,11] Furthermore, Dozier, Kim, and Chaikin[12] concluded in their forced Rayleigh scattering measurement that the self-diffusion constant of the water-soluble dye actually decreased in the conducting regime of the phase diagram. The other possible mechanism is the possible distortion of the spherical droplets at the percolation temperature into rodlike micelles which have lower percolation limits. Depolarized light scattering and flow birefringence measurements fail to support this conjecture. Furthermore, viscosity measurements, as well as SANS data in the percolation region, showed no abnormalities as may be expected from the structure change. The question of the rate of surfactant resident time on the droplet interface is not known to any great detail, but it is expected to be in the microsecond range, roughly consistent with the observed onset of frequency dependence of the conductivity.

The authors are grateful for the capable experimental assistance of Wayne Gallegher, and they have greatly benefited from discussions with Sam Safran, Gary Grest, Shobo Bhattacharaya, and Jim Stokes.

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