Theory and Experiment of Electrical Conductivity and Percolation Locus in Water-in-Oil Microemulsions

C. Cametti,$^{(1)}$ P. Codastefano,$^{(1)}$ P. Tartaglia,$^{(1)}$ J. Rouch,$^{(2)}$ and S. H. Chen$^{(3)}$
$^{(1)}$*Dipartimento di Fisica, Universitá di Roma La Sapienza, Piazzale A. Moro 2, I-00185 Roma, Italy*
$^{(2)}$*Centre de Physique Moléculaire Optique et Hertzienne, Université de Bordeaux I,*
351 Cours de la Libération, 33405 Talence CEDEX, France
$^{(3)}$*Department of Nuclear Engineering and Center for Materials Science and Engineering,*
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 6 October 1989)

An extensive set of measurements of low-frequency conductivity σ of a three-component microemulsion system, AOT-water-decane, as a function of temperature and volume fraction of the dispersed phase has been made. σ can be calculated at low ϕ by means of a charge-fluctuation model, while it can be interpreted for higher values of ϕ in terms of power-law behavior. The percolation locus in the ϕ-T plane has been determined starting from the vicinity of the lower consolute point up to $\phi=0.65$. This line can be successfully interpreted in terms of a modified version of the analytical theory of percolation given by Xu and Stell.

PACS numbers: 82.70.Kj

The AOT(surfactant)-water-decane(oil) three-component microemulsion (AOT denotes sodium di-2-ethylhexylsulfosuccinate) is an ideal system for studying electrical-conductivity percolation phenomena since throughout the isotropic one-phase region it forms a water-in-oil microemulsion. A water-in-oil microemulsion can be effectively considered as a heterogeneous two-component system made up of conducting spherical droplets of water, coated by a monolayer of surfactant molecules, immersed in a continuous nonconducting oil medium. From a liquid-state-physics point of view a water-in-oil microemulsion, can be considered as a collection of conducting hard spheres interacting among themselves via an attractive potential. There has been a number of experimental[1-6] and theoretical[7-10] studies of electrical-permittivity and -conductivity percolation phenomena in the literature in this AOT-based model microemulsion system over the last few years. In particular, we have recently experimentally established the validity of dynamic scaling for the dielectric relaxation phenomena.[6] As far as the static conductivity percolation is concerned, the picture that emerges from the experiments is as follows: The low-frequency conductivity σ (below 100 kHz) has a power-law behavior with exponents which are different below and above the percolation threshold. At a given volume fraction of the microemulsion droplets ϕ, a temperature threshold T_p exists above which there is a dramatic increase in the conductivity. On the other hand, at a given temperature, there exists a volume-fraction threshold ϕ_p above which the system has high conductivity. Kim and Huang[2] showed that ϕ_p and T_p are uniquely related to each other. The locus of percolation points in the T-ϕ plane, which we shall simply call the percolation line, seems to originate from the vicinity of the cloud-point curve (the critical temperature is about 40 °C and the critical volume fraction about 0.1) and extends to the lower temperatures as the volume fraction increases.[11] The exponent below the threshold has a value $s'=-1.2$ and above the threshold a value $t=1.94(6)$. s' is called the dynamic percolation exponent which was predicted by Grest *et al.*[10] based on the theory of dynamic percolation and was later confirmed by Kim and Huang.[2] On the other hand, t is called a static percolation index and was calculated by Derrida *et al.*[12] using renormalization-group methods and was also experimentally confirmed by many authors.[2-6]

Bug, Safran, and Grest,[13] in an attempt to understand the existence of the percolation line, performed Monte Carlo simulations on square-well fluids. By adjusting the depth and the width of the square-well potential, they were able to produce the percolation line in the vicinity of and below the spinodal curve. Seaton and Glandt[14] performed a Monte Carlo simulation on a slightly polydisperse adhesive-sphere system and showed the existence of the percolation line. Very recently, Xu and Stell[15] solved analytically for the locus of the percolation threshold, using a model hard-sphere system with an attractive Yukawa tail in the mean spherical approximation. They introduced a pair-connectedness function and constructed and solved the Ornstein-Zernike equation for this function. By integrating the pair-connectedness function one can calculate the average cluster size S. The condition for percolation comes from requiring S to become divergent. The thermal part of this theory always produces an upper consolute point and the associated spinodal curve, since it is a theory for simple fluids with a fixed potential function. However, the AOT-based microemulsion system is known to show a lower-consolute-point phenomenon.[16] For this to happen, the strength of the attractive Yukawa potential needs to be a temperature-dependent quantity. Chen and co-workers[17] have previously obtained the temperature dependence of the strength parameter for the AOT microemulsion system and have also obtained the spinodal curve corresponding to the lower consolute point.

In this paper we report first an extended set of measurements of low-frequency conductivity of the AOT-water-decane system at a molar ratio [water]/[AOT] =40.8, in the one-phase region, for the whole range of temperatures from 10 °C to 50 °C and volume fractions from 0.098 to 0.65. We analyzed the dc conductivity as a function of temperature, for all volume fractions, using the charge-fluctuation model of Eicke, Borkovec, and Das-Gupta[18] for data much below the percolation threshold. In the vicinity of the threshold we analyzed the data using power laws. Finally, we applied a modified version of the theory of Xu and Stell,[15] taking into account the temperature-dependent interaction potential, and have successfully accounted for the experimentally measured percolation line.

The electrical conductivity of the water-in-oil microemulsions was measured at a frequency of 10 kHz by means of a HP4192A impedance analyzer in connection with a temperature-controlled parallel-plane capacitance cell. The cell constants were obtained using solutions of known conductivity and permittivity. The electrodes were plated with platinum black in order to reduce the electrode polarization. The microemulsions were prepared by mixing appropriate fractions of deionized, low-conductivity water ($\sigma < 10^{-6}\ \Omega^{-1}\mathrm{cm}^{-1}$ at 20 °C) and reagent-grade decane, using surfactant AOT from Sigma Co. without further purification. According to our experience the purity of the surfactant will shift the cloud-point curve and the percolation line, at a given volume fraction, in the same direction without changing the relative temperature distance. At the molar ratio 40.8 the microemulsion-droplet water core has a size distribution of the Schultz type with an average size of 50 Å and a polydispersity of 30%, as determined by previous small-angle neutron-scattering experiments.[19] The hydrodynamic radius of the microemulsion droplets has also been determined by a dynamic light-scattering experiment, and is of the order of 85 Å.[20] The average size and the size distribution do not change, at a given temperature, as a function of volume fraction.

Figure 1 shows a log-linear plot of the ratio σ/ϕ as a function of temperature for all the volume fractions we studied. One immediately sees that the conductivity follows a sigmoidal curve with the lower portion of the curves converging to a common straight line, nearly horizontal. This is precisely the prediction of the charge-fluctuation model of Eicke *et al.*[18] As the temperature increases, at a given volume fraction, the percolation phenomenon sets in and the conductivity increases by more than 4 orders of magnitude. Finally, the conductivity saturates for all values of the volume fractions, reaching a value corresponding to the infinite-cluster limit of the static percolation.

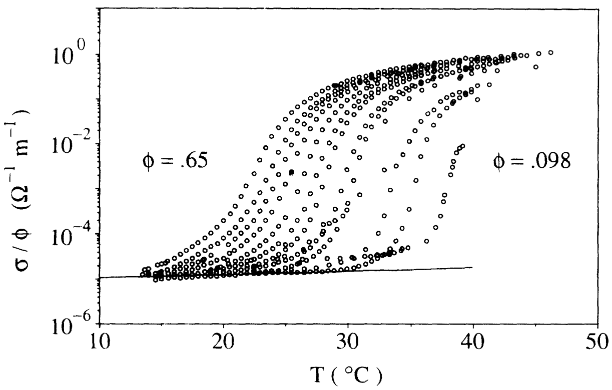

FIG. 1. The measured conductivity σ/ϕ as a function of temperature for the following volume fractions (from right to left): ϕ=0.098, 0.125, 0.150, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65. The solid line represents the locus of Eq. (1).

The charge-fluctuation model we are referring to[18] explains the excess conductivity of the microemulsion over that expected for the nonpolar solvents, decane in our case, up to 10 orders of magnitude, in the regime of very dilute microemulsions. The average charge of a microemulsion droplet is zero, since the number of negative ions of the surfactant molecule is on the average balanced by the positive counterions in the water core. The charge fluctuations may be due to the transient migration of the sodium counterions or the surfactant anions away from the droplet, which causes a net charge z to be produced. The conductivity is then equal to $\sigma = ne^2\langle z^2\rangle/6\pi\eta r$, which assumes that the charge transport is mediated by Stokes-Einstein diffusion of the charged sphere of net charge ze and number density n, in a solvent of shear viscosity η. The mean-square charge fluctuation $\langle(ze)^2\rangle$ is then evaluated from the thermodynamic fluctuation theory in conjunction with Born's theory of ionic solvation to obtain $\langle z^2\rangle = \epsilon r k_B T/e^2$, where ϵ is the permittivity of decane. In this model the conductivity is independent of r, but its ratio to the volume fraction, the specific conductivity, is given by

$$\frac{\sigma}{\phi} = \frac{\epsilon k_B T}{8\pi^2 \eta r^3}\,. \tag{1}$$

All the quantities appearing in Eq. (1) are accurately known from other experiments and allow a precise evaluation of σ. Since free diffusion of the droplets is assumed, we expect this theory to be valid only in the low-volume-fraction limit. The solid line in Fig. 1 refers to an evaluation of Eq. (1) with the values of ϵ and η for pure decane[21] and the radius of the droplets equal to 100 Å. The agreement between the fluctuating-charge model and our data is quite good for the measurement taken at low volume fraction over more than 15° in temperature. The range of validity of the theory reduces as ϕ increases, even though the low-temperature limit of the conductivity seems to approach the theoretical value.

For a polydisperse system of spheres the r^3 in Eq. (1) should be replaced by $\langle r^3 \rangle$. For a Schultz distribution of sizes, $\langle r^3 \rangle = 1.3\langle r \rangle^3$, leading to an effective hydrodynamic radius of 91 Å. This value is very close to the result of dynamic light scattering, which is approximately 85 Å.

In Fig. 2 we report the analysis of our measurements in terms of the power laws of dynamic and static percolation. We plot the scaled conductivities $T_p(\sigma/A)^{-1/s}$ and $T_p(\sigma/B)^{1/t}$, where A and B are the amplitudes of the anomalies, as a function of the distance $T-T_p$ for each volume fraction. The percolation threshold has been located approximately at first from the inflection point of the curve σ vs T and then successively refined by means of a nonlinear least-squares analysis which also gives the exponents $s' = 1.2 \pm 0.1$ and $t = 1.9 \pm 0.1$. The percolation thresholds as a function of T and ϕ determined in the two ways agree very well with one another. The agreement with the static percolation theory above the threshold is very good for all cases. The deviations from the dynamic percolation behavior below T_p are more evident for data at low volume fractions. The deviation from the power-law behavior shows up at a distance in temperature from T_p which becomes increasingly smaller. However, precisely in this region the charge-fluctuation model fully explains the experimental results.

In Fig. 3 we show, in a T-ϕ plane, with open circles, the locus of lower cloud points and, with solid circles, the locus of the percolation threshold determined above. Below the cloud points the microemulsion exists in an isotropic one-phase state and to the right of the percolation locus it is in a highly conducting state. The thin solid line is the locus of spinodal points, corresponding to the lower cloud points, calculated using an interdroplet potential consisting of a hard core plus an attractive Yukawa tail. The thick solid line and the dashed line are the percolation lines calculated using the second and third models of the theory of percolation introduced by Xu and Stell. In this theory three models are considered. The first one is referred to as connectedness with certainty, where two particles are considered to be directly connected if the distance between the centers is within a given distance. The second and third models are referred to as connectedness in probability and are defined in terms of the probability of two particles at a given distance apart being connected. In transcribing the latter theory to make it applicable to the lower-consolute-point phenomena, as in the case of AOT-based microemulsions, we explicitly take into account the temperature dependence of the interaction strength of the Yukawa potential:

$$\beta u(x) = -Ke^{-z(x-1)}/x \quad (x > 1)\,, \tag{2}$$

where $\beta = 1/k_BT$, x is the interdroplet distance divided by the diameter of the droplet $2r$, z is the range of the potential in units of $2r$, and the strength parameter K is taken as

$$Ke^z = K_0 + K_1T + K_2T^2\,. \tag{3}$$

We choose the parameters such that $z = 0.73$, $K_0 = -0.0329$, $K_1 = 0.013$, $K_2 = 2.124 \times 10^{-4}$, and T is expressed in °C. This is an empirical relation obtained by Chen and co-workers[17] in fitting small-angle neutron-scattering data of the same microemulsion system taken in the critical region. In using the percolation-in-probability approach of Xu and Stell we choose the parameters $K^+ = \lambda K$ for the second model, $K^+ = -\exp(\lambda K)$ for the third model, and $z^+ = z$, with the parameter $\lambda = 0.45$. It is amazing that the model of Xu and Stell, when combined with the empirical relation,

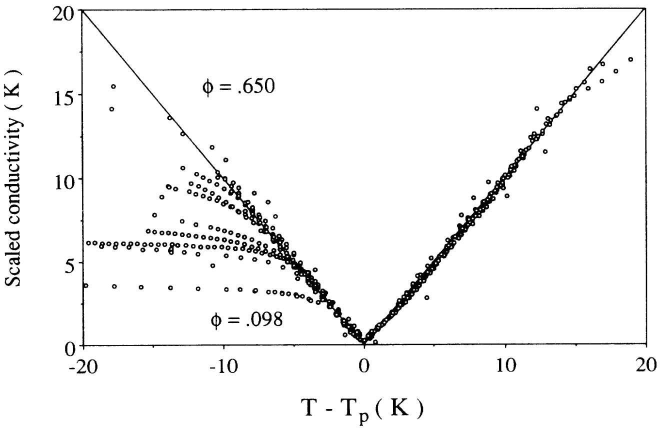

FIG. 2. The scaled conductivities (defined in the text) for all volume fractions plotted as a function of $T-T_p$. Solid lines represent the power laws below and above the threshold.

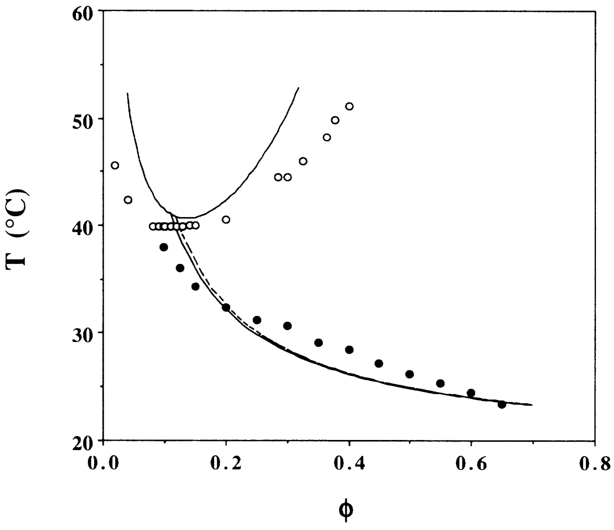

FIG. 3. The experimentally determined cloud-point curve (open circles) and percolation line (solid circles) compared to the computed spinodal line (thin solid line) and percolation locus for the second (thick solid line) and the third model (dashed line) of Xu and Stell.

Eq. (3), produces such a quantitative agreement with the experimental percolation locus. The first model of Xu and Stell gives a steep percolation line going from the theoretical critical point at $\phi_c = 0.137$ and $T_c = 40.6$ °C to the hard-sphere limit $\phi_{\rm HS} = 0.144$ at low temperature for a particle distance equal to $2.2r$ and $z = 0.73$.

In conclusion, we have shown clear evidence that the charge-fluctuation model of conductivity is applicable in ionic microemulsions at low volume fractions, and the power-law behavior near the percolation point is well obeyed above the threshold for all volume fractions, but the range of validity below the threshold is increasingly limited as the volume fraction decreases. We have explained the locus of percolation line in the T-ϕ plane, for the first time, using the percolation-in-probability models of Xu and Stell, suitably modified to take into account the temperature dependence of the interaction strength.

We are grateful to Professor George Stell and Dr. J. Xu for informative discussions on the theory used in this paper and Dr. John Huang for showing us his unpublished results on the percolation line. The work of S.H.C. was supported by a grant from the National Science Foundation. The financial support to the Italian authors comes from Gruppo Nazionale di Struttura della Materia, Consiglio Nazionale delle Ricerche, and Centro Interuniversitario di Struttura della Materia, Ministero della Pubblica Istruzione. J.R. and S.H.C. are grateful to the Department of Physics, University of Rome, for the hospitality during the course of this work. Centre de Physique Moléculaire Optique et Hertzienne is unité associé No. 283 du CNRS.

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

[2] M. W. Kim and J. S. Huang, Phys. Rev. A **34**, 719 (1986).

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

[4] J. Peyrelasse, M. Moha-Ouchane, and C. Boned, Phys. Rev. A **38**, 4155–4161 (1988).

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

[6] C. Cametti, P. Codastefano, A. DiBiasio, P. Tartaglia, and S. H. Chen, Phys. Rev. A **40**, 2013 (1989).

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

[8] J. M. Luck, J. Phys. A **18**, 2061 (1985).

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

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

[11] J. S. Huang (private communication).

[12] B. Derrida, D. Stauffer, H. J. Hermann, and J. Vannimenus, J. Phys. (Paris), Lett. **44**, L701 (1983).

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

[14] N. A. Seaton and E. D. Glandt, J. Chem. Phys. **86**, 4668 (1987).

[15] J. Xu and G. Stell, J. Chem. Phys. **89**, 1101 (1988); G. Stell, J. Phys. A **17**, L855 (1984).

[16] J. S. Huang and M. W. Kim, Phys. Rev. Lett. **47**, 1462 (1981).

[17] S. H. Chen, T. L. Lin, and M. Kotlarchyk, in *Surfactant in Solutions,* edited by P. Bothorel and K. Mittal (Plenum, New York, 1987), Vol. 2; S. H. Chen, T. L. Lin, and J. S. Huang, in *Physics of Complex and Supramolecular Fluids,* edited by S. A. Safran and N. A. Clark (Wiley, New York, 1987).

[18] H. F. Eicke, M. Borkovec, and B. Das-Gupta, J. Phys. Chem. **93**, 314 (1989).

[19] M. Kotlarchyk, S. H. Chen, J. S. Huang, and M. W. Kim, Phys. Rev. A **28**, 508 (1983); **29**, 2054 (1984).

[20] J. Rouch, A. Safouane, P. Tartaglia, and S. H. Chen, J. Chem. Phys. **90**, 3756 (1989).

[21] *American Institute of Physics Handbook* (McGraw-Hill, New York, 1972), 3rd ed.