Model disordered media provided by ternary microemulsions

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Variation of component ratios in a class of ternary microemulsions is shown to give model media of prescribed microstructure. Observed structural changes are analyzed in the context of a percolative phenomenon. The effective medium approximation predicts measured transport properties. Near percolation, transport properties are consistent with scaling characteristic of a static percolation transition. The system therefore allows *independent* measurement of transport and mechanical properties in a well-characterized disordered medium.

The prediction of transport and mechanical properties in a disordered medium requires an accurate characterization of the microstructure. While a large body of work exists on theories and simulations to predict geometric and transport properties of disordered media [1], no *well-characterized* three-dimensional experimental system has so far been available to test these predictions. Moreover, no system studied allowed the independent measurement of transport and mechanical properties. We show that ternary microemulsions formed from double-chain quarternary ammonium surfactants with oil and water provides such a system [2–6]. The system most studied comprises didodecyl dimethyl ammonium bromide (DDAB), water, and a C_6–C_{12} alkane. DDAB is essentially insoluble in both alkanes and in water, and is therefore constrained to reside at the oil-water interface [7]. This circumstance allows determination of microstructure relatively easily. The microemulsion is bicontinuous through most of the single phase region as inferred from conductivity [2,3,8], diffusivity [5], and small-angle scattering [9] studies. At high water content the system undergoes a structural transition to disconnected water droplets in oil.

An explicit random geometric model, the disordered-open-connected cylinders (DOC) model [8] gives a *parameter-free* interpretation of the microstructure. The DOC model is an analytic approximation to a surface of constant curvature. The topology of the interface is not fixed. The microstructure exhibited by the interface can vary from random monodisperse spheres to highly interconnected structures. The approximation to the actual surface is a network of droplets connected (on average) to Z nearest neighbors by cylindrical segments. The approximation leads to analytic expressions for the surface area and volume of the internal phase enclosed by the interface [8]. The model yields a unique density of sphere centers n and coordination number Z characterizing the liquid structure for a known water volume fraction, internal surface area, and effective surfactant parameter [10]. Small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS) spectra as well as conductivity, viscosity, and diffusivity data are quantitatively consistent with the predicted structure [9].

We analyze the microstructural transition of the microemulsion system in the context of percolative phenomena. The DOC model is used to predict the transition from bicontinuous oil-water to a disconnected water-in-oil phase. The percolation transition point is in agreement with that deduced from conductivity and diffusivity data. The experimental conductivity and diffusivity measurements are compared with a theoretical treatment based on effective medium theory. The microemulsion exhibits behavior consistent with static percolation. The scaling behavior of the transport and mechanical properties near the microstructural transition is consistent with a static percolative system.

Microemulsion structure is uniquely constrained by the local and global packing constraints of a surfactant molecule at the oil-water interface. This shape is characterized by an effective packing parameter [10] of the surfactant molecule which includes absorbed oil in the surfactant tails. If v is the surfactant molecular volume (including oil uptake), a is the area of the head group, and l is the tail length, the packing parameter is defined as $(v/al)_{\rm eff}$. The effective parameter is determined by energetics and can be inferred from the phase diagram [6]. The values used in this study are given in Table I. The packing parameter $(v/al)_{\rm eff}$ is assumed constant throughout the L_2 phase. As the oil swollen volume of the surfactant and extended chain length are fixed, the only possible variable is the area per molecule. SAXS data confirm that this is also constant across the entire microemulsion phase region. We calculate the variation of the coordination number Z and density of sphere centers, n, with water content for all the oils listed in

TABLE I. Values of the effective surfactant parameter [6] in the presence of different oils used in this study. (These values predict the phase boundaries of the microemulsion.)

Oil	Hexane	Octane	Decane	Dodecane	1-Decene
$\left[\dfrac{v}{al}\right]_{\rm eff}$	1.28	1.18	1.15	1.12	1.18

Table I at various surfactant-to-oil (S/O) ratios. The values for n derived by the model are in agreement with small-angle scattering data [9]. In all cases, the connectivity of the interface varies smoothly throughout the L_2 region. Figure 1 shows the experimentally measured specific conductance [2,3] and the theoretically predicted coordination number as a function of water content for typical sets of experimental data.

Voronoi cells for random hard-sphere packings have an average number of bonds about each vertex of 13.4. In the DOC model an average number Z of these bonds radiating from each vertex is sheathed with cylinders, and is open to transport and conduction. If Z is large, the network is well connected. At some well-defined value of Z defined as Z_c, the percolation threshold, there is a transition in the topological structure of the random network from a well-connected structure to a disconnected one. The bond percolation threshold for the Voronoi tesselation with average coordination of 14 is $p_c = 0.0956$ [11]. We approximate the percolation threshold of the DOC network by $Z_c = 13.4 p_c \approx 1.3$.

Consider the observed conductivity variation as a percolation transition. The DOC model predicts that the coordination of the three-dimensional (3D) random networks decreases upon water dilution (see Table II and Fig. 1). The initial decrease in coordination leads to a slow drop in the conductivity, followed by an abrupt decrease in the conductivity at high water content due to the loss of continuous paths through the water region of the microemulsion. The model prediction for the conducting-nonconducting transition point $(Z \approx 1.3)$ is in excellent agreement with the experimentally observed transition from a conducting to a nonconducting medium (cf. Fig. 1 and Table II). The quantitative prediction of the structural transition point illustrates the efficacy of this sample parameter-free characterization of the microemulsion structure.
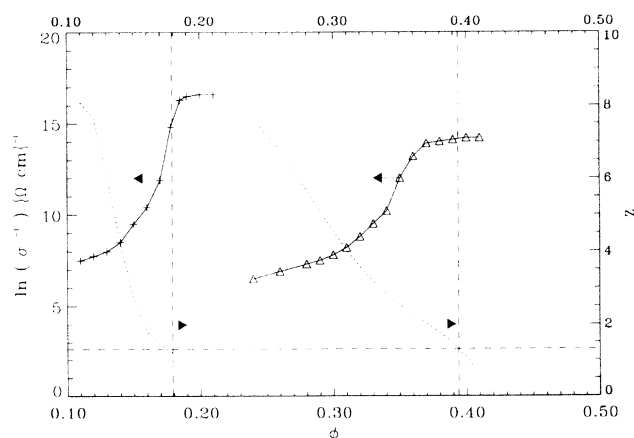
TABLE II. Experimental quantities [2] and model prediction for the system DDAB-octane-water with a surfactant-to-oil ratio equal to 0.176 and an effective surfactant parameter $(v/al)_{\text{eff}} = 1.18$. Compositions and measured quantities for the sample are given in the first through fourth columns. The fifth and sixth columns give the parameters resulting from a fit to the DOC model, where r_s is the sphere radius and Z the coordination number.

ϕ_{water}	ϕ_{int}	Σ (Å^{-1})	$-\ln(\sigma)$ (Ω^{-1} cm^{-1})	r_s (Å)	Z
0.12	0.106	0.008 67	7.75	44	8.1
0.13	0.113	0.008 60	8.0	46	7.5
0.14	0.121	0.008 53	8.5	49	6.45
0.15	0.129	0.008 45	9.0	50	3.7
0.16	0.137	0.008 37	10.4	52	2.9
0.17	0.145	0.008 30	12.2	54	1.9
0.178	0.152	0.008 23	14.8	57	1.4
0.185	0.157	0.008 18	16.3	58	1.1
0.19	0.161	0.008 14	16.5	60	1.05
0.20	0.169	0.008 06	16.6	63	0.5
0.21	0.177	0.007 98	16.6	67	0.25

A careful study of NMR self-diffusion has been carried out on the ternary microemulsion DDAB-dodecane-water at various surfactant-to-oil (S/O) ratios [4,5]. Results of these studies mirror the conductivity studies—the water self-diffusion coefficients are found to be highly concentration dependent and to exhibit regions where water molecules are confined to small domains, the water self-diffusion constant varying by up to two orders of magnitude upon dilution. The predicted variation of the coordination number Z with water content is shown in Fig. 2 along with the measured diffusivity. The self-diffusion constant reduces significantly as the coordination number decreases.

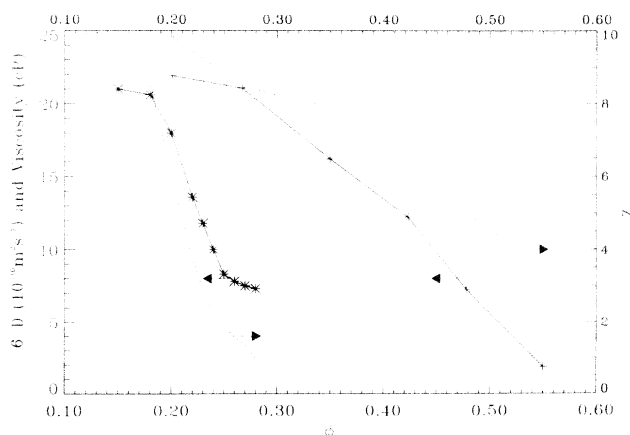Viscosity data for octane and decane microemulsions

FIG. 1. Experimentally measured [2,3] conductance data and theoretically predicted coordination number Z as a function of water content. The solid curve passes through the conductance data. The dashed lines give the model prediction for the coordination number. The threshold $Z_c \approx 1.3$ is shown along with the prediction for the conduction transition point. ($\times$) Octane [$(S/O)_{\text{weight}} = 0.176$]; ($\triangle$) 1-Hexene [$(S/O)_{\text{weight}} = 0.667$].

FIG. 2. Experimentally measured diffusivity [5] and viscosity [2] data, and theoretically predicted coordination number Z as a function of water content. ($+$) Dodecane diffusivity [$(S/O)_{\text{weight}} = 0.185$]; ($*$) Octane viscosity [$(S/O)_{\text{weight}} = 0.293$]. The solid curve passes through the experimental data. The dashed line gives the average coordination number.

was obtained along water dilution lines in the L_2 region [2]. The microemulsions exhibit a high viscosity in the bicontinuous low-water content region, which decreases steadily as water is added. The minimum in the viscosity curve coincides with the conductivity transition [12]. The variation of the coordination number Z as a function of water content is summarized in Fig. 2. A general trend of reduced viscosity as the coordination number decreases is evident.

Model predictions based on an effective medium approximation (EMA) for the conductance and diffusive properties of the microemulsions are now compared with experiment. Kirkpatrick [13] showed that for a network of coordination number Z, the EMA predicts that $f(g)(g-\sigma_e)/(g+A\sigma_e)dg=0$ where $A=Z/2-1$. The pore conductance distribution $f(g)$ is given by $f(g)=p_o\delta(g-g_o)-p_i\delta(g-g_i)$, where p_i is the fraction of bonds in the internal phase defined by $p_i=Z/13.4$, Z is given by the solution to the DOC model, and $p_o=1-p_i$. The brine conductivity g_i and the oil conductivity g_o are taken to be asymptotic values (see Fig. 1) of the conductivities of the microemulsion at $Z=Z_{max}$ and $Z=0.0$, respectively. In Fig. 3, the prediction of the effective medium theory is compared with the experimental data across the full range of the conductivity measurements. The agreement is good in all cases.

The effective medium theory for resistor network can also be used to find the effective diffusivity of a random medium [14]. Replacing g_i by the asymptotic diffusivity measured at high coordination number and setting $g_o=0$ allows a prediction of the effective water self-diffusivity D_w in the microemulsion phase. This prediction of the EMA is also compared with experiment in Fig. 3. The quantitative prediction of the transport (conductive and diffusive) properties near the microstructural transition is a further indication of the accuracy of the DOC description of ternary microemulsion structure.

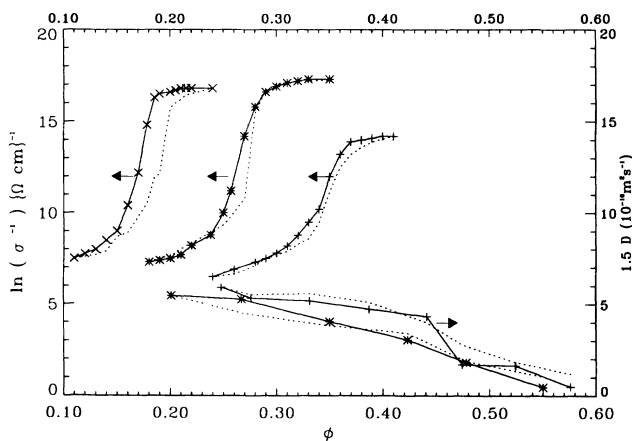Of particular interest in the study of transport in, and

FIG. 3. Comparison of the experimental conductance and diffusive data (solid curve) with the EMA prediction (dashed curve): Conductivity: ($\times$) Octane [$(S/O)_{weight}=0.176$]; ($\ast$) Decane [$(S/O)_{weight}=0.250$]; ($+$) 1-Hexene [$(S/O)_{weight}=0.667$]. Diffusivity: ($\ast$) Dodecane [$(S/O)_{weight}=0.333$]; ($+$) Dodecane [$(S/O)_{weight}=0.441$].

mechanical properties of, disordered media, is the behavior of properties in the vicinity of the percolation threshold [15]. For example, the behavior of the effective conductivity of the percolative medium near $p_c(=Z_c/13.4)$ is described (for $p>p_c$) by $\sigma_e=(p-p_c)^{\mu_E}$ where μ_E is a critical exponent. Theoretically, the exponent μ_E is presumed to depend only on the dimensionality of the medium. Numerous theoretical studies and numerical calculations provide a currently accepted value of the conductivity exponent, $\mu_E \simeq 2.0$ [15]. From the coordination number Z given by the DOC model and the experimental conductivity data, we can evaluate μ_E for the microemulsion. The values of the critical exponents derived from the data are given in Table III. The experimental data are indeed in agreement with the predicted values for static percolation; $\mu_E \simeq 2.0$. The behavior of the effective diffusivity D_e of the microemulsion near p_c is also of interest. Since D_e is proportional to σ_e, D_e has the same power law dependence on p near p_c. The value of the exponent derived from the diffusivity data is given in Table III. The behavior is again consistent with a static percolative system.

There is interest in the rheological behavior of chemical gels near the sol-gel transition [16]. Experimental measurements indicate that near the gel transition, the viscosity η diverges with an exponent k [$\eta \sim (p-p_c)^{-k}$]. The value of k can be either in the range 0.6–0.8 [17] or 1.3–1.5 [18] depending upon experimental conditions. In the former case the behavior of the system can be described by a static percolation network [19]. The exponent k describing the divergence of the octane and decane microemulsion viscosity near the threshold ($Z_c \approx 1.3$) is $k \approx 0.40(\pm 0.2)$ and $k \approx 0.75(\pm 0.2)$ consistent with a static percolation system.

It should be noted that the rheological properties of a sol-gel transition are different from the properties of a ternary microemulsion at the structural transition. In the gel transition the viscosity *diverges* as the percolation threshold is approached from *below* [$\eta \sim (p-p_c)^{-k}$ for $p<p_c$]. In our system k describes the increase in the viscosity *above* the transition [$\eta \sim (p-p_c)^k$ for $p>p_c$]. The percolation model developed to explain the viscosity divergence in the sol-gel system [19] supposes that the behavior of η below p_c is described by a *superelastic* percolation network. In contrast, the DDAB system is analogous to an ordinary elastic percolation network, which yields an elastic exponent k in the range 3.5–3.8. It is not yet clear how to interpret the scaling behavior of the viscosity of the DDAB system.

In summary, we have discussed the microstructural transition of the ternary DDAB-alkane-water microemulsion in the context of percolative phenomena. The simple, parameter-free (DOC) interpretation of the microstructure is found to predict the percolative transition point accurately. Experimentally measured transport properties compare well with a simple effective medium treatment. The scaling of the transport properties is consistent with a static percolative transition.

Ternary microemulsions have previously been studied as model percolative media. Several investigations of the

TABLE III. Values of the conductivity (a) and diffusivity exponents (b) derived from the experimental data [2,5]. The theoretical prediction for the conductivity and diffusivity exponent is $\mu_E = \mu_D \simeq 2.0$. Surfactant-to-oil ratio (S/O) is by weight.

	(a) Conductivity		
Hexane	Octane	Decane	1-Decene
$1.6\pm0.3(S/O=0.253)$	$1.8\pm0.2(S/O=0.176)$	$1.8\pm0.2(S/O=0.250)$	$2.3\pm0.2(S/O=0.250)$
$1.6\pm0.5(S/O=0.441)$			$2.2\pm0.2(S/O=0.667)$

(b) Diffusivity
Dodecane

$1.4\pm0.4(S/O=0.185)$
$1.85\pm0.4(S/O=0.333)$
$1.85\pm0.4(S/O=0.441)$

ternary water-AOT-oil microemulsion [20–24] appear to confirm that this system exhibits a *dynamic* percolation behavior [25,26]. The characterization of the microstructure of the AOT microemulsions near the transition is problematic, however; the behavior of the AOT-oil-water system is not simply dependent on the volume fraction of the internal phase, but depends as well on an unknown interaction range, on the salt content [24], and on the solubility of AOT in oil [7]. Effective transport properties in these systems can only be interpreted *qualitatively* within the framework of a percolative system [24]. Describing the structural transition observed in DDAB ternary microemulsions as a static percolative transition is controversial. Microemulsions are in many cases notoriously labile systems. The DDAB system has, however, been deliberately designed. DDAB is virtually insoluble in water and oil and is therefore constrained to reside at the oil-water interface. This circumstance allows one to understand the microstructure relatively easily. The DDAB-C_6-C_{12}-water system exhibits a wide range of mi-crostructure which can be *predicted* from elementary concepts. This allows one to *tune* experimental variables to give a specific microstructure and allows the independent determination of the conductivity, diffusivity, and viscosity [12]. The ternary DDAB-(C_6-C_{12})-water system is a most appropriate candidate for the experimental study of transport in disordered media. Recent water self-diffusion measurements [27] in ternary DDAB microemulsions exhibit anomalous (time dependent) behavior in agreement with a static percolative system [28]. Finally, ternary microemulsion systems monomer-water-DDAB have been shown to exhibit a predictable microstructure and have been polymerized to produce a solid porous material with a well-defined microstructure [29]. This enables the study of flow, dispersion, and displacement processes.

[1] M. Sahimi, Rev. Mod. Phys. 65, 1393 (1993).
[2] S. Chen, D. Evans, and B. Ninham, J. Phys. Chem. 88, 1631 (1984).
[3] B. Ninham, S. Chen, and D. Evans, J. Phys. Chem. 88, 5855 (1984).
[4] F. Blum, S. Pickup, B. Ninham, S. Chen, and D. Evans, J. Phys. Chem. 89, 711 (1985).
[5] K. Fontell, A. Ceglie, B. Lindman, and B. Ninham, Acta Chem. Scand., Ser. A 40, 247 (1986).
[6] S. Hyde, B. Ninham, and T. Zemb, J. Phys. Chem. 93, 1464 (1989).
[7] D. Evans, D. Mitchell, and B. Ninham, J. Phys. Chem. 90, 2817 (1986).
[8] T. Zemb, S. Hyde, P.-J. Derian, I. Barnes, and B. Ninham, J. Phys. Chem. 91, 3814 (1987).
[9] I. Barnes et al., J. Phys. Chem. 92, 2286 (1988).
[10] D. Mitchell and B. Ninham, J. Chem. Soc. Faraday Trans. 2 77, 601 (1981).

[11] G. Jerauld, L. Scriven, and H. Davis, J. Phys. C 17, 3429 (1984).
[12] C.-M. Chen and G. Warr, J. Phys. Chem. 96, 9492 (1992).
[13] S. Kirkpatrick, Rev. Mod. Phys. 45, 573 (1973).
[14] H. Davis, J. Am. Ceram. Soc. 60, 499 (1977).
[15] D. Stauffer, and A. Aharony, Introduction to Percolation Theory, 2nd ed. (Taylor & Francis, London, 1992).
[16] D. Stauffer, A. Coniglio, and M. Adam, Adv. Polym. Sci. 44, 105 (1982).
[17] M. Adam, M. Delsanti, and D. Durand, Macromolecules 18, 2285 (1985).
[18] J. Martin, D. Adolff, and J. Wilcoxin, Phys. Rev. Lett. 61, 2620 (1988).
[19] S. Arbabi and M. Sahimi, Phys. Rev. Lett. 65, 725 (1990).
[20] S. Bhattacharya, J. Stokes, M. Kim, and J. Huang, Phys. Rev. Lett. 55, 1884 (1985).
[21] M. Kim and J. Huang, Phys. Rev. A 34, 719 (1986).
[22] M. Moha-Ouchane, J. Peyrelasse, and C. Boned, Phys.

Rev. A **35**, 3027 (1987).

[23] J. Peyrelasse and C. Boned, Phys. Rev. A **41**, 938 (1990).

[24] J. Peyrelasse, C. Boned, and Z. Saidi, Phys. Rev. E **47**, 3412 (1993).

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

[26] G. Grest, I. Webman, S. Safran, and A. Bug, Phys. Rev. A

33, 2842 (1986).

[27] M. Knackstedt, M. Monduzzi, and B. Ninham (unpublished).

[28] S. Havlin and H. Ben-Avraham, Adv. Phys. **36**, 695 (1987).

[29] B. Ninham, S. Hyde, and R. Pashley, Formation of porous materials, US Patent Pending, 1992.