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Reverse micelle to sponge phase transition

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A pseudoternary system exhibiting a single-phase domain extending from water-in-decane to sponge phase to decane-in-water microemulsions as temperature and decane weight fraction (α; relative to brine+decane) are varied has been studied by Chen, Chang, and Strey [J. Chem. Phys. **93**, 1907 (1990)]. Conductivity and self-diffusion measurements at 45 °C show that the reverse micelle to sponge phase transition proceeds in a sequence of two continuous transitions defined quantitatively by an order parameter. This is the first study to quantify the *onset* of sponge phase formation within a single-phase domain, as a function of composition, and to quantify the *amount* of sponge phase. © *1997 American Institute of Physics.* [S0021-9606(97)51918-0]

I. INTRODUCTION

A variety of studies have shown that isotropic single-phase microemulsion domains may be transformed from water-in-oil to sponge phase (bicontinuous) to oil-in-water microstructure by varying one or more field variables such as temperature, concentration, or disperse phase volume fraction.[1–8] By sponge-phase microstructure we mean interpenetrating tubules of oil and water separated by a monolayer of surfactant.[9] The pseudoternary brine (0.6% w/w aqueous NaCl), AOT [sodium bis(2-ethylhexyl) sulfosuccinate], and decane system has been carefully characterized[6] using small-angle neutron scattering (SANS), and can be viewed in terms of the Shinoda diagram in Fig. 1. At high α in the lower right corner and at low α in the lower left corner of Fig. 1, water-in-oil microemulsions exist. At low α and high temperature, an oil-in-water microemulsion exists. Paths within this single-phase domain connecting these two water-in-oil microemulsion regions with the oil-in-water region must pass through a sponge-phase region of low to zero mean curvature. Chen, Chang, and Strey[6] produced a cartoon illustrating how these transformations might be imagined to occur. Starting in the water-in-oil regions, separated droplets are presumed to form clusters that progressively grow. These clusters are imagined to then transform into bicontinuous sponge-phase microstructures. These sponge-phase structures are thought to then transform further into a continuous aqueous phase containing clusters of oil-swollen micelles that dissociate into isolated oil-in-water droplets. The present report is devoted to a conductivity and NMR-based self-diffusion study of the transformation of this pseudoternary system. It develops an order-parameter characterization that distinguishes cluster formation and sponge-phase formation as separable components of percolation.

II. EXPERIMENT

We examined this system along the 45 °C isotherm from $\alpha=1–0.3$. Microemulsions were prepared by weight from the respective chemical components. AOT was obtained from Fluka, spectroscopic grade decane was obtained from Eastman Laboratory Chemicals, and these components were used without further purification. Low frequency conductivity measurements at 45 °C were made with a Yellow Springs Instruments conductivity meter. NMR self-diffusion measurements of water, AOT, and decane were made at 45 °C on a Varian Inova 400, wide bore (89 mm) spectrometer operating with a ^{1}H frequency of 400.0 MHz. The spectrometer was equipped with a 5 mm, indirect detection, pulsed field gradient accessory capable of achieving up to 33 G cm^{-1}.

III. RESULTS AND DISCUSSION

Electrical conductivity data are illustrated in Fig. 2. The initial decrease is due, we believe, to decreasing mobility of charge carriers (surfactant aggregates) as water nucleates larger micelles (see subsequent self-diffusion data and discussion). It appears the onset of conductivity percolation occurs at about $\alpha=0.85$. The conductivity increases two orders as α decreases from 0.85 to 0.70 (brine *increases*), and increases another two and a half orders as α decreases to 0.30.

Self-diffusion data for decane, water, and AOT are plotted in Fig. 3. Decane self-diffusion decreases gradually as α decreases to 0.3. Water and AOT diffusion dramatically decrease as α decreases from 1 to 0.85. The very large self-diffusion for AOT observed at high α indicates that reverse micelles in this system with no or with very little water exist as very small aggregates. These aggregates coalesce and
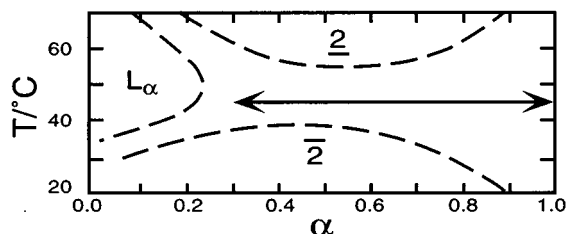

FIG. 1. Phase diagram of brine (0.6% w/w aqueous NaCl), AOT (12% w/w), and decane pseudoternary system as a function of temperature (T) and decane weight fraction (α; relative to decane+brine). A single-phase domain extends to higher and lower temperatures as α approaches 1 and branches to high and low temperature as α approaches 0.
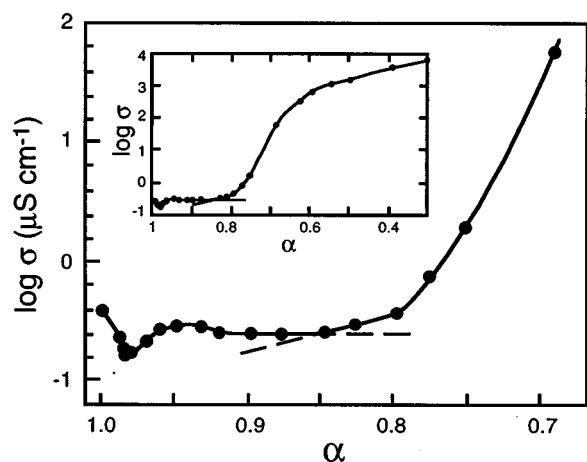
FIG. 2. Low frequency conductivity σ at 45 °C as a function of α for brine, AOT, and decane microemulsions. A distinct breakpoint at $\alpha=0.85$ corresponds to the onset of percolation in electrical conductivity.

grow as more water is added, and as a consequence, the corresponding self diffusion of water and AOT in these swollen micelles decreases.

At $\alpha=0.85$ a breakpoint in the AOT self diffusion is evident. This diffusion decreases further with decreasing α, but the slope is distinctly different than on the other side of this breakpoint. A breakpoint in the water self diffusion is also seen at $\alpha=0.85$. However, the water self-diffusion increases with further decreases in α. This increase in water self-diffusion correlates directly with a breakpoint in the conductivity data at the same α (Fig. 2), and may be taken as an indication of the *onset* of electrical conductivity percolation. This increasing water self-diffusion and decreasing AOT self-diffusion is consistent with the model of cluster
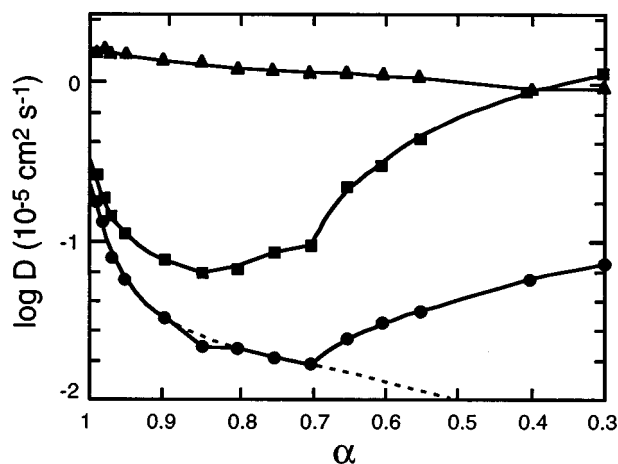

FIG. 3. Self-diffusion coefficients at 45 °C for water (■), decane (▲), and AOT (●) in ternary brine, AOT, and decane microemulsions as a function of composition α (weight fraction of decane relative to decane and brine). The dotted curve is a double exponential decay fit to the AOT self-diffusion data for $\alpha \geqslant 0.7$.

formation put forth, where fractal like clusters are presumed to provide a path for increased conductivity.[6,10]

At $\alpha=0.7$ additional breakpoints in both water and AOT self-diffusion are evident. Water self-diffusion increases much more markedly below $\alpha=0.7$ than above, and at about $\alpha=0.4$ the water self-diffusion equals (crosses) the decane self-diffusion. This crossing point corresponds, approximately, to a composition where the water and decane are present at equal *volume* fractions, and is taken as an indication that the predominant microstructure present is a sponge-phase bicontinuous microstructure of essentially zero mean curvature. The upturn in AOT self-diffusion as α decreases below 0.7 shows that coincidentally with a more pronounced increase in water self-diffusion, is the onset of dramatically increasing AOT self-diffusion. We assign this upturn to the *onset* of formation of sponge-phase microstructure.

In the percolation regime in α of 0.85–0.7 the self-diffusion of AOT is apparently *retarded* by the monolayer intermolecular forces and the *de facto* bilayer barrier that necessarily must exist locally at contact between pairwise associated droplets. Extended or enhanced AOT self-diffusion requires inversion of an AOT through the hydrophobic bilayer tail region, in order to move from droplet to droplet. In a sponge-phase microstructure, however, an AOT needs only overcome the barrier to exit the monolayer into the pseudocontinuous aqueous phase, where the AOT is then free to diffuse along the AOT-aqueous interface at a rate much faster than droplet self-diffusion.

The observed self-diffusion of water at α greater than 0.4 should not be taken as the respective swollen micellar diffusion without considering the solubility and molecular diffusion of this component in the decane pseudocontinuous phase. The molecular diffusion of water in decane at 45 °C was measured as 0.93×10^{-5} cm^2 s^{-1}. With this estimate of water molecular diffusion, the observed self-diffusion data for water may be analyzed according to a two-state approximation depicted by Eq. (1),[11]

$$D_{obs} = xD_c + (1-x)D_m, \tag{1}$$

where D_c represents diffusion in the decane pseudocontinuous phase and D_m represents diffusion contributed by translation of swollen micelles. The variable x represents the mole fraction of water in the pseudocontinuous phase.

The value of D_m varies as the micelles swell with decreasing α. As a first approximation, we take D_m to be represented by the observed self-diffusion of AOT for $\alpha \geqslant 0.7$. The AOT self-diffusion data for $\alpha \geqslant 0.7$ were fitted to a double exponential decay function in generating the dotted curve in Fig. 3. In this approximate treatment, we take D_m to be represented by the exponential tail of this fitted function for $\alpha < 0.7$. With these values for D_c and D_m, the apparent mole fraction of water x in the pseudocontinuous phase is calculated from Eq. (1) and the water self-diffusion data of Fig. 3. The resulting values are illustrated in Fig. 4.

These mole fraction results illustrate several distinct regimes. For $\alpha \geqslant 0.85$, x decreases as reverse micelles are growing and decreasing in number. At about $\alpha=0.85$, x begins to increase, and it increases markedly as α decreases
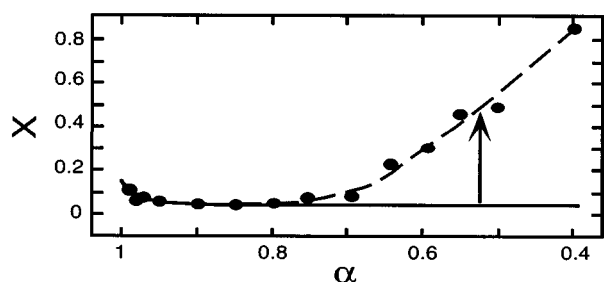
FIG. 4. Apparent mole fraction (x) of water in continuous phase derived from two-state model [Eq. (1)] for water diffusion. The solid curve represents a single exponential (decay) fit to the x values obtained for $\alpha \geqslant 0.85$. The dotted curve fitted to the data for $\alpha \leqslant 0.85$, is provided as a guide to the eye. The arrow illustrating the separation between the exponential tail and the dotted curve represents $\hat{x}$, the apparent excess mole fraction of water in the continuous phase.

further. This increase is illustrated by the dashed curve in Fig. 4. The *difference* between the solid curve and the dashed curve in Fig. 4, and illustrated there by the arrow, is taken as $\hat{x}$, the apparent *excess* mole fraction of water in the continuous phase. From a pseudophase perspective, such an excess is inconsistent with partitioning between the pseudocontinuous phase and the swollen micellar phase. We assign this excess, $\hat{x}$, to water populating percolating clusters and sponge-phase water channels.

We define an order parameter S for quantifying water in these percolating clusters and sponge-phase channels relative to the total disperse phase water, including water in the swollen micellar pseudophase:

$$S = \frac{\hat{x}}{1 - x + \hat{x}} . \qquad (2)$$

This order parameter varies continuously between 0 and 1, and is illustrated in Fig. 5. The denominator represents the total disperse phase water. In Fig. 5, point a corresponds to a continuous transition, where this order parameter first deviates from zero, to the onset of electrical conductivity increase and percolation, to the onset of water self-diffusion increase (Fig. 3), and to the onset of percolating cluster formation. Point b corresponds to a *second* continuous transition, to
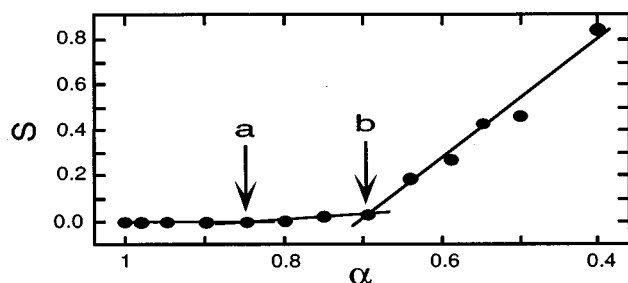

FIG. 5. Order parameter (S) for disperse phase distribution of water. Point a corresponds to the onset of electrical conductivity increase, the beginning of percolation, and to the onset of increase in water self-diffusion. Point b corresponds to the onset of increase in AOT self-diffusion, and to the onset of sponge phase formation.

dramatically increased water self-diffusion, to the onset of surfactant self-diffusion increase, and to the onset of sponge-phase formation.

This order parameter appears essentially piecewise linear over these three different regimes in composition. For $\alpha \geqslant 0.85$ it is identically zero. For $0.85 \geqslant \alpha \geqslant 0.7$ it increases linearly as percolating clusters form. For $0.7 \geqslant \alpha$ it increases very rapidly and linearly, as the microstructure transforms to sponge phase. Independent SANS data[6] unequivocally show essentially zero mean curvature at $\alpha = 0.4$. This composition also corresponds to equal volume fractions of decane and brine, to equal diffusivity of water and of decane, and depicts a bicontinuous sponge-phase microstructure. The linearity of the order parameter connecting this $\alpha = 0.4$ composition to the continuous transition at point b supports this assignment of sponge-phase formation commencing at b.

These conductivity and self-diffusion studies provide independent experimental support for the mechanism and picture of reverse micelle to fractal cluster to sponge-phase transformation put forward by Chen, Chang, and Strey.[6] Clusters appear as intermediates in the formation of sponge phase from isolated droplets. A related transformation was suggested earlier,[10] where a linear cluster of percolating swollen micelles was pictured as transforming into an open water channel spanning the length of the linear cluster.

Having put forward this two-stage mechanism of sponge-phase microstructure formation, we point to other supporting data. Geiger and Eicke[12] used self-diffusion and conductivity as we have in examining T-driven percolation in a water, AOT, isooctane microemulsion. The onset water self-diffusion increase coincided with increasing conductivity, at about 305 K. Between 305 and 321 K the AOT self-diffusion decreased, and at 321 K it began to increase. An analogous water-in-isooctane system was examined by Jonströmer, Olsson, and Parker,[13] the onset of percolation and water self-diffusion was observed at 19 °C, and a subsequent increase in AOT self-diffusion occurred at 26 °C. Feldman et al.[14] examined a water, AOT, decane system without added salt and reported percolation (also T-driven) and self-diffusion of the chemical components. The water self-diffusion increased markedly at 19 °C, at about the same temperature that the electrical conductivity began to increase. AOT diffusion did not markedly increase until 28 °C. These systems may be modeled by the same two-stage process of cluster formation marked by the onset of percolation and increasing water self-diffusion and sponge-phase formation marked by the onset of increasing AOT self-diffusion.

It appears that the present results provide a direct experimental method for separately *mapping* the onset of percolation *and* the onset of sponge-phase formation. We stress that it is not the analytical percolation threshold that we map here, but the *onset* of percolation as indicated by the onset of increased water self-diffusion, as this increase coincides with increasing electrical conductivity. While general agreement has been reached that single-phase microemulsions having approximately equal volume fractions of oil and aqueous pseudophases and exhibiting essentially equal relative diffusivities of oil and water are bicontinuous sponge-phase mi-

croemulsions, the quantitative onset of this transformation has not heretofore been mapped. Furthermore, the order parameter approach described herein provides explicit means for *quantifying* the chemical equilibria involved in the onset and growth of sponge-phase microstructure.

ACKNOWLEDGMENTS

[1] P. Guering and B. Lindman, Langmuir **1**, 464 (1985).

[2] M. T. Clarkson, D. Beaglehole, and P. T. Callaghan, Phys. Rev. Lett. **54**, 1722 (1985).

[3] J. O. Carnali, A. Ceglie, B. Lindman, and K. Shinoda, Langmuir **2**, 417 (1986).

[4] M. Borkovec, H.-F. Eicke, H. Hammerich, and B. Das Gupta, J. Phys. Chem. **92**, 206 (1988).

[5] R. T. Hamilton, J. F. Billman, and E. W. Kaker, Langmuir **6**, 1696 (1990).

[6] S. -H. Chen, S.-L. Chang, and R. Strey, J. Chem. Phys. **93**, 1907 (1990).

[7] K. Shinoda, M. Araki, A. Sadaghiani, A. Khan, and B. Lindman, J. Phys. Chem. **95**, 989 (1991).

[8] R. Strey, Colloid Polym. Sci. **272**, 1005 (1994).

[9] L. E. Scriven, Nature **263**, 123 (1976).

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

[11] B. Lindman and U. Olsson, Ber. Bunsenges. Phys. Chem. **100**, 344 (1996).

[12] S. Geiger and H.-F. Eicke, J. Colloid Interface Sci. **110**, 181 (1986).

[13] M. Jonströmer, U. Olsson, and W. O'Neil Parker, Jr., Langmuir **11**, 61 (1995).

[14] Y. Feldman, N. Kozlovich, I. Nir, N. Garti, V. Archipov, Z. Idiyatullin, Y. Zuev, and V. Fedotov, J. Phys. Chem. **100**, 3745 (1996).