Molecular Diffusion in a Microemulsion

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(Received 7 November 1984)

Pulsed-field-gradient NMR was used to examine translational diffusion of the oil, water, and surfactant components in a microemulsion. The diffusion of both oil and water shows a smooth variation along a line in the phase diagram where two-phase/three-phase/two-phase transitions are encountered, and the diffusion is unrestricted and three dimensional. Dynamic structural effects are needed to interpret the results. Surfactant diffusion reaches a peak in the three-phase region.

PACS numbers: 82.70.Kj, 66.10.Cb

The phase diagram of oil-brine-surfactant mixtures with an alcohol added as cosurfactant can show a variety of domains. In particular, it can show with increasing brine salinity S a transition from a two-phase region, in which a microemulsion of oil droplets in water is in equilibrium with essentially a pure oil phase, to a three-phase region where the microemulsion is in equilibrium with both essentially pure oil and pure water phases, to a second two-phase region where the microemulsion, now water droplets in oil, is in equilibrium with essentially a pure water phase.

Our understanding of the structure of the microemulsion in the two- and three-phase regions is still incomplete. In some microemulsion systems, recent small-angle neutron scattering studies[1] have determined the structure factor associated with microemulsion droplets, and indicate a short-ranged attractive interaction between the droplets. Eicke, Shepherd, and Steinemann[2] have proposed a model for coalescence of droplets.

In the system under study here, as we have mentioned, in the two-phase regions the microemulsion is thought[3] to consist of droplets surrounded by the surfactant, moving about with Brownian motion in the continuous phase of the excess component. On approaching the three-phase boundary the droplets are thought[3] to grow in size, with a percolation transition in the vicinity of the boundary so that in the three-phase region the microemulsion is "bicontinuous." Bicontinuous structures were first proposed by Scriven.[4] The alcohol is thought[5] to be adsorbed between the hydrocarbon tails of the surfactant molecules at the oil/water interface, increasing the fluidity of the interface. Other important and related properties are the growth in turbidity[6] and the decrease in the diffusion coefficient[7] (see Fig. 1) measured in static and dynamic light-scattering studies on the approach to the three-phase boundary, both of which are characteristic of a second-order critical phase transition, while the volume of the third phase in the three-phase region decreases continuously to zero at the phase boundary,[6] a property which is characteristic of a first-order phase transition. Widom[8] in a recent paper on a "model" microemulsion has suggested that the phase transitions are "critical points for second-order phase transitions" in Landau and Lifshitz's technology.[9]

To give further information on the structure of these microemulsions and the nature of the phase transitions we have measured the translational self-diffusion of oil, water, and surfactant molecules using the pulsed-field-gradient NMR technique through the entire two-three-two–phase system. In this technique,[10,11] the NMR "echo" signal of the various species is observed in the presence of a pulsed magnet-

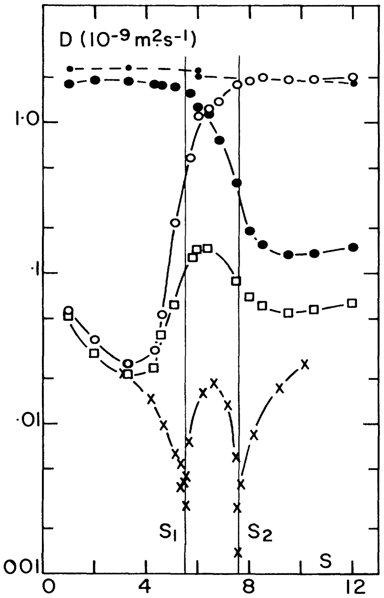

FIG. 1. Molecular diffusion coefficient vs brine salinity for oil (open circles), water (solid circles), and surfactant (squares) in the microemulsion. Points represent an average of different samples and observation times Δ. Also shown are values (small dots and dashed lines) for oil (water) in the oil (water) phase, and light-scattering data (crosses, see text). The full lines are a guide to the eye.

ic field gradient, and if the molecules diffuse to a new position during the observation time Δ then the echo is attenuated, and a measurement of this attenuation yields an effective diffusion coefficient D. Since values of Δ can be varied between 1 and 100 msec, this leads to a sensitivity to diffusion over distances between 100 nm and 10 μm (for typical values of D). Chemical-shift resolution between the oil, water, and surfactant proton NMR signals enables diffusion coefficients to be determined for these separate molecular species.

If the molecules undergo unrestricted three-dimensional diffusion then their mean square displacement is $r^2 = 6D\Delta$ and D is independent of Δ.[12] This has been found to be the case for oil and water diffusion in all samples, but the signal was too weak to check this for the surfactant molecules. Comparison of the relative signal intensities with the known microemulsion composition[7] shows consistency in component ratios. The strengths of the individual signals are consistent with all of the oil and water molecules contributing to the signals.

At the extremes of the two-phase regions the measured values of D are close to those determined by light-scattering techniques, which is characteristic of the Brownian motion of droplets. As the phase boundaries are approached, rather than decreasing as observed by light-scattering techniques, the molecular diffusion coefficient increases smoothly to a value of free molecular diffusion in the corresponding continuous phase. No anomalies occur at the phase boundaries. These results, as we will discuss later, show the importance of the dynamical structural interactions between the droplets by way of random coalescence and breakups, which allow the contained molecules to sample all space and so give a three-dimensional diffusion law.

The system we have studied is that used by Pouchelon *et al.*[6,7] in their light-scattering studies, namely (percent by weight indicated) toluene (47.25%), brine (water + NaCl) (46.80%), sodium dodecyl sulfate (SDS, 1.99%), and butanol cosurfactant (3.96%). The temperature has been controlled at $27 \pm 2\,^\circ$C. The phase boundaries occur at $S_1 = 5.5$ and $S_2 = 7.6$ (with salinity S in weight percent of NaCl in brine solution), while the midpoint of the three-phase region occurs at $S_0 = 6.45$. (This is an estimate of the point where the equilibrium oil-surfactant-water interface has no preferential curvature.[13])

The NMR data for diffusion within the microemulsion are shown in Figs. 1 and 2, along with values for diffusion within the associated oil and water phases, and values of D determined by Pouchelon[7] using dynamic light-scattering techniques (the latter are generally on a time scale of 10–100 μs). The two determinations of D at the extremes of the data at high and low salinities give nearly the same values, but very different behavior is observed in the mid regions. If we consider the data for the oil molecules, it is reasonable to assume that at low S the oil is held within the droplet, and its motion is then given by the Brownian motion of the droplet: Droplet sizes ~10 nm with $\eta \sim 1$ cP lead to $D \sim 10^{-11}$ m^2 s^{-1} as observed. A decrease of D is then observed, corresponding to a growing size for the droplet, but by $S = 4$ the molecular diffusion coefficient increases steadily. The corresponding behavior is found for the water molecules with decreasing S.

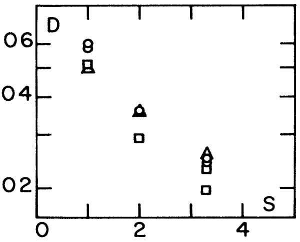

FIG. 2. Detail from Fig. 1, showing typical reproducibility of results. Each circle (square) represents the measurement on oil (surfactant) for a sample, $\Delta = 10$ ms. Triangles represent values for oil at $\Delta = 100$ ms.

The diffusion coefficient for the SDS molecules is also close to the corresponding droplet value at the extremes of the two-phase regions, but rises to a symmetrical peak at S_0. (The symmetry of the data about S_0 is revealed by plotting $D\eta$ vs $1-x$, where $x = S/S_0$ for $S < S_0$, $x = S_0/S$ for $S > S_0$, which takes into account the differing viscosities η of oil and water.)

The observation that oil (or water) and surfactant D values lie above the Brownian droplet values, along with their independence of the time interval Δ, indicates clearly that the oil (or water) and surfactant are able to move further than the droplets. This is only possible if random directional coalescences between the droplets occur, providing additional distances for motion. Where the coalescence time is sufficient for complete molecular redistribution, this leads to an effective diffusion coefficient $D = D_{\mathrm{droplet}} + \frac{1}{6} n_c R^2$ where n_c is the number of coalescences per second, R is the combined droplet radius.

The coalescences at low and high salinities will be due to collisions arising from the Brownian motion, giving $n_c = 8\pi D_{\mathrm{droplet}} R n$ (Smoluchowski[14]), where n is the number of droplets per unit volume, while near the phase boundaries at larger volume fractions, fluctuations in the droplet shape may also contribute to the coalescence rate and to the dimensions over which molecules may move during molecular redistribution. Safran[15] has published a theory on fluctuations of microemulsion droplets. Estimates of $n_c R^2$ suggest that spherical droplet coalescence will explain the difference between droplet and molecular diffusion in the extreme two-phase regions, since this term leads to $D \simeq D_{\mathrm{droplet}}(1 + c_v)$, where the droplet volume fraction $c_v \sim 0.1$. However, near the three-phase region the differences are so large that significant shape fluctuations are implied. Where these fluctuations are large (and slow), the extent to which the droplet molecules may displace will be limited by the local (intradroplet) diffusion rate. We would expect that in such a region, the effective D of the surfactant and droplet molecules would show a difference. Such a difference is apparent in our data.

The oil and water D values at the phase boundaries and at S_0 are approximately $\frac{1}{3}$ and $\frac{2}{3}$ of the free diffusion values, pointing to locally one-dimensional and two-dimensional random pathways at these points. (Locally confined motion still leads to $r^2 = 6D\Delta$, with a reduced value for D.[12]) Such a model would imply that the surfactant molecular diffusion, which at S_0 is comparable to amphiphile diffusion along a lamellar surface,[16] would also differ by a factor of 2 between S_0 and the phase boundaries. This is indeed what we observe.

In summary, oil and water molecules in the microemulsion, observed over times of 10 and 100 ms, show unrestricted three-dimensional diffusion throughout the entire two-three-two–phase system. On approach to the three-phase region the measured molecular diffusion coefficients, including those for the surfactant, rise above the Brownian droplet values determined by dynamic light scattering. This increase in molecular diffusion towards the free-molecular values of the corresponding continuous phase, or in the surfactant case towards a peak in the three-phase region, shows no anomaly through the phase boundaries. Coalescence and breakup of droplets is needed to interpret these results. The data presented here therefore support the coalescence model proposed by Eicke, Shepherd, and Steinemann.[2]

Following the submission of this paper, Dr. D. Langevin has sent us a preprint[17] which reports a similar but less complete study of the variation of D in this system.

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