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Critical Behavior in Inverse Micelle Systems

J. P. Wilcoxon*

*Organization 1153, Sandia National Laboratories, Albuquerque, NM 87185

Abstract:

We report measurements of the critical behavior of an inverted micelle system. The two component system consists of a nonionic surfactant n-decyl octaoxyethylene glycol monoether ($C_{10}E_8$) in a hydrocarbon, dodecane. The system has an upper critical consolute point at 30±2 wt% $C_{10}E_8$ at a temperature of $T=28.05 \pm 0.03$. We demonstrate both static and dynamic scaling is obeyed with universal 3D-Ising exponents describing the divergence of the osmotic compressibility and the static correlation length.

Introduction:

The microstructure of oil continuous nonionic *inverted* micelle systems has not been investigated to the same degree as water continuous normal micelle systems and is considerably less well understood. However, the macroscopic phase behavior of oil-continuous $CH_3(CH_2)_{i-1}(OCH_2CH_3)_jOH$ (hereafter abbreviated C_iE_j) nonionic surfactant systems and their corresponding microemulsions (water added) has been investigated and shown to be quite fascinating.[1] These systems consist of surfactant aggregates (micelles) with hydrophobic tail groups facing an oil-continuous medium. Like their non-inverted micelle counterparts, these systems are of great technical importance as phase-transfer catalysts, microemulsion polymerization media, and as media for the formation of submicron catalytic particles.[2] In contrast to normal micelles which typically have lower critical consolute points in an experimentally accessible range, inverse micelles consist of a single homogeneous phase at high temperatures which separates into two phases as the temperature is reduced. However, phase separation is not always observed before the freezing point of the solvent unless a fairly hydrophilic surfactant is combined with a reasonably hydrophobic oil.

In the case of the surfactant family C_iE_j, the ratio of i/j controls the phase separation temperature, since this ratio determines the compatibility of a given surfactant/hydrocarbon system. Low ratios result in high phase separation temperatures, while fixing i/j and increasing the length k of the hydrocarbon C_k to make it more hydrophobic will also increase the upper critical consolute point.

Results and Discussion:

What is known concerning the microstructure of inverse micelle systems? Like their normal micelle counterparts, small angle neutron scattering (SANS) measurements demonstrate that nonionic inverse micelle systems consist of surfactant aggregates as shown in figure 1. However, in most cases the aggregation numbers are considerably smaller, on the order of 10-50 molecules as compared to 50-100 with Guinier radii R_g as shown,. For strongly hydrophobic surfactants (e.g. $C_{12}E_3$), sizes are smaller still (i.e. <10 Å), and geometric considerations as well as SANS confirm that the micelle structure is not spherical, as is the case with many nonionic normal micelles. However, if critical fluctuations dominant the scattering, the exact micelle structure should be irrelevent and the long-wavelength scattering should exhibit the universal aspects well established for normal micelle systems.

Due to the importance of O_2 and H_2O exclusion in these systems, we used Aldrich Gold label degassed dodecane which is also shipped sealed under argon with a septum cap and is extracted using airless techniques into the scattering vial. The scattering vials were either 10 or 16 mm outer diameter and were flame sealed after freezing (i.e.to prevent explosion), under dry argon. The critical temperatures were then found to be stable for many months. All glassware was extensively cleaned and oven dried to prevent introduction of water into the system.

We now discuss the application of static and dynamic light scattering to study static and

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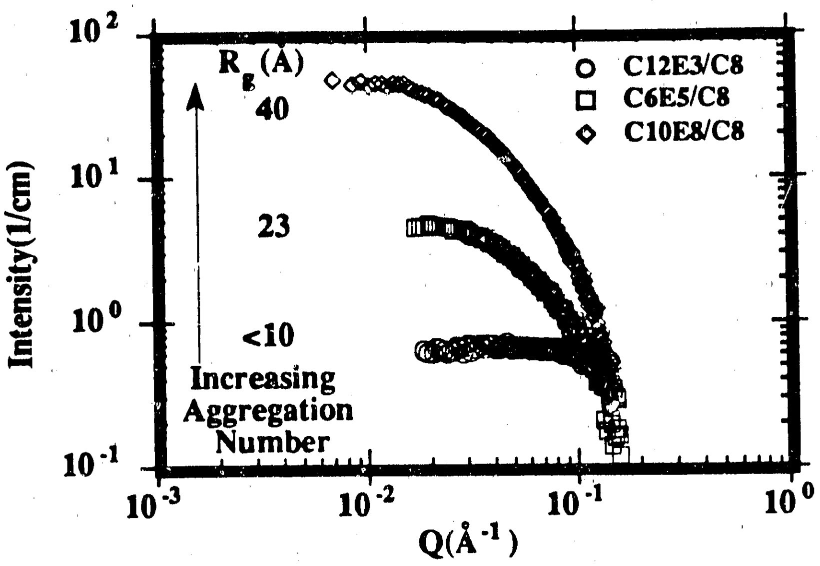

Figure 1. Small angle neutron scattering intensity vs momentum transfer, Q for three nonionic surfactants, C_iE_j *of increasing aggregation number, in the same solvent, deuterated octane,* C_8.

dynamic scaling in the $C_{10}E_8/C_{12}$ system. We have also investigated C_6E_5/C_{16} and C_7E_5/C_{14} and these results are very similiar. In our measurements the total range of momentum transfer was $.00025<Q<.005$ Å^{-1} (corresponding to length scales between 20 nm and 500 nm).

We found that only a single length scale is required to explain our static light scattering data from this system. Wedemonstrated that theintensity depends on the momentum transfer Q ($Q=4\pi n\sin(\theta)/\lambda$, where n is the refractive index) as

$$\frac{I(0)}{I(Q)} = 1 + (Q\xi)^2 \qquad (1)$$

This simple description with a single length scale $\xi(\varepsilon)$, the static correlation length, accurately describes this data. It turns out that equation (1) also describes the scattering of $C_{10}E_8/C_{12}$ samples whose concentration differs from the critical value. Two principal differences are observed for off-critical surfactant concentrations though. The first difference is that $\xi(\varepsilon)$ shows an apparent divergence with ε but only over a finite range (i.e. ξ becomes constant near T_{cp}). The second difference is that ξ is smaller for off-critical concentrations at each ε. These observations agree with our previous studies of normal micellar solutions.[3,4]

By analyzing our static light scattering data using equation (1) we obtained values of I(0) and ξ as a function of ε. I(0) is proportional to the osmotic compressibility and since both dn/dc and n vary insignificantly over the temperature and concentration, c, range (~5 °C) of this study we plot I(0) directly vs ε in Figure 2. Five values of the surfactant concentration are shown. As for normal micelle systems,[3,4] there is no evidence that either I(0) or ξ ever saturates on the critical isochore in this system. As mentioned in the previously paragraph, the off-critical surfactant concentrations diverge only over a finite range of ε, and accordingly, only these points showing a power-law divergence in ε are used to obtain the apparent slopes shown in figure 2. On the critical isochore the data obeys $I(0)\sim\varepsilon^{-\gamma}$, with the value of $\gamma=1.25\pm0.05$, in good agreement with the 3D Ising prediction of $\gamma=1.24$. For off-critical surfactant concentrations, the exponent γ has a mean field (~1.0) or smaller values. Our uncertainties in γ are based upon sample-to-sample reproducibility.

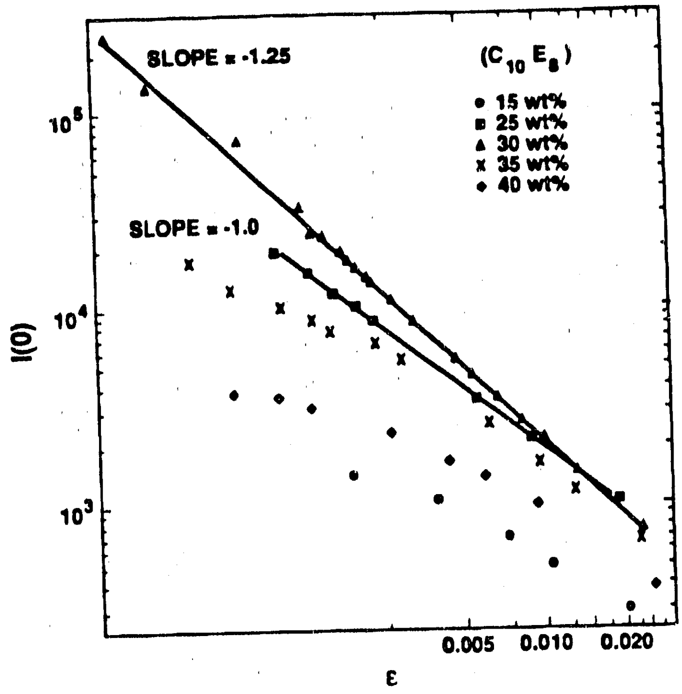

Figure 2. The intensity at zero momentum transfer I(0), (arbitrary units), vs the reduced temperature $\varepsilon=(T_{cp}-T)/T_{cp}$ *for the* $C_{10}E_8$*/dodecane system. The weight percent* $C_{10}E_8$ *is indicated in the figure.*

We also investigated the divergence of ξ with ε for several surfactant concentrations. On the critical isochore the data follow the power law $\xi \sim \xi_o \varepsilon^{-\nu}$, with $\nu=0.64 \pm .04$, in agreement with the 3D Ising prediction of $\nu=0.63$. The range of interaction indicated by $\xi_o=6.0$ Å is smaller than that observed for normal micelle solutions[3,4] which typically have values of 10-20 Å depending on the surfactant. For off-critical surfactant concentrations the exponent ν becomes mean field ($\nu=.5$) or smaller in value. Within experimental error we find $\gamma=2\nu$ for all concentrations for which an apparent diverence in I(0) and ξ is observed. For surfactant concentrations far off-critical ξ is independent of ε. These observations are exactly as expected if critical fluctuations dominate the scattering.

To test the scaling of the relaxation of the concentration fluctuations as the critical point is approached we made measurements of the intensity autocorrelation function. We found that within ~5 °C of the critical temperature, (this spans our entire range of ε), this function is a single exponential, consistent with similar observations on both binary fluid systems and normal micelles. Thus this system is described by a single characteristic heterodyne relaxation time τ from which we can compute an apparent diffusion constant $D_{app}(Q)=1/(2*Q^2*\tau)$. Mode-mode coupling theories predict that $D_{app}(Q)$ should follow the form $D_{app}(Q)=k_B T K(Q\xi)/6\pi\eta\xi$, where $\eta(T)$ is the macroscopic shear viscosity as measured in a low-shear capilliary viscometer, k_B the Boltzmann constant, ξ the measured correlation length, and $K(x=Q\xi)$ is the Kawasaki function,

$$K(x)= (3/4x^2)[1 + x^2 + (x^3 - x^{-1})\tan^{-1}x]. \qquad (2)$$

K(x) is known to be a universal function describing data from a wide variety of binary fluid

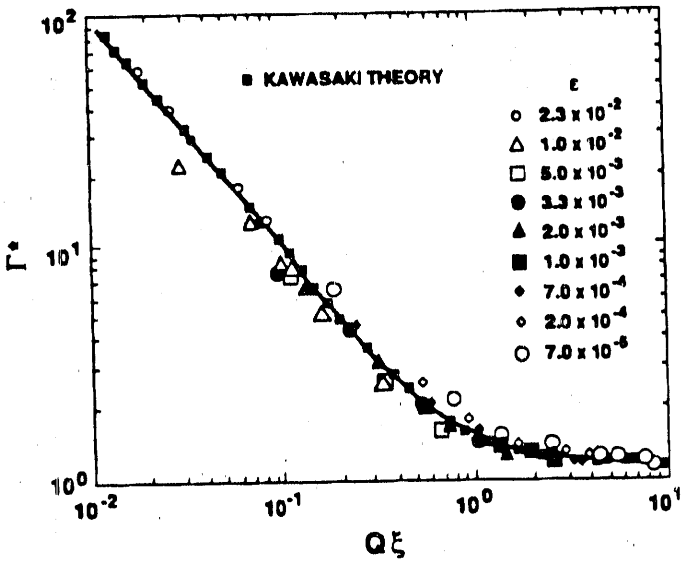

Figure 3. Scaled Rayleigh linewidth Γ^* vs the product of the momentum transfer, Q and the static correlation length ξ, as a function of reduced temperature ε, for the $C_{10}E_8/C_{12}$ system on the critical isochore, 30 wt% $C_{10}E_8$.

systems, and we have shown it also describes data from several normal nonionic micelle solutions.[3,4] Since it has no adjustable parameters it is an exacting test of dynamic scaling in a critical system. Figure 3 shows data for several values of ε on the critical isochore. The data are plotted as values of the reduced Rayleigh linewidth $\Gamma^*=D_{app}(6\pi\eta\xi/k_BT)$ vs $Q\xi$. Shown as a solid line in the same figure is the Kawasaki prediction. Several values of ε are indicated in this figure. The agreement is excellent.[5]

In conclusion, we have demonstrated static and dynamic scaling in an inverted micelle system. Ising exponents are observed on the critical isochore with mean field or weaker divergence on either side. Dynamic scaling following the simple Kawasaki mode-mode coupling prediction is also observed.

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4. J. P. Wilcoxon and E.W. Kaler, J. Chem. Phys., **86**, 4684, (1987).
5. Data obtained for off-critical surfactant concentrations also shows evidence for critical slowing near the cloud point temperature with D(0) diverging as a power law with Ising type exponents, but D(Q) does not have the angular dependence predicted by (2).

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