SURFACTANT-BASED CRITICAL PHENOMENA IN MICROGRAVITY

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ABSTRACT

The objective of this research project is to characterize by experiment and theoretically both the kinetics of phase separation and the metastable structures produced during phase separation in a microgravity environment. The particular systems we are currently studying are mixtures of water, nonionic surfactants, and compressible supercritical fluids at temperatures and pressures where the coexisting liquid phases have equal densities (isopycnic phases). In this report, we describe experiments to locate equilibrium isopycnic phases and to determine the "local" phase behavior and critical phenomena at nearby conditions of temperature, pressure, and composition. In addition, we report the results of preliminary small angle neutron scattering (SANS) experiments to characterize microstructures that exist in these mixtures at different fluid densities.

INTRODUCTION

Ground-based measurements of surfactant solutions undergoing phase separation where density differences between the coexisting phases are minimized provide an excellent guide for defining key measurements and systems for study in shuttle experiments where density differences are irrelevant. Our approach has been to employ compressible supercritical fluids and use pressure as a field variable to match phase densities, and to use surfactants to slow the rate of phase separation to allow easy observations. Moreover, because two equilibrium phases containing different surfactants can have markedly different viscosities, these mixtures will make possible examination of the role of rheology in setting metastable structures during phase separation. A practical motivation for matching densities with a supercritical fluid at elevated pressures, rather than a liquid solvent, is to examine a variety of polymerization processes in microemulsion and micellar phases where the supercritical fluid can be polymerized; butadiene, for example, would be a potential supercritical fluid for such polymerizations.

In the following, we present current results of calculations to predict state points corresponding to isopycnic phases and experiments to locate them for the three-

component mixture: water, carbon dioxide, and the ethoxylated alcohol surfactant, C_8E_5. Small-angle neutron scattering (SANS) measurements were also made on mixtures of the surfactant $C_{12}E_6$, CO_2, and D_2O to probe for the presence of aggregates in these solutions. These experimental results are also reported.

EXPERIMENTAL WORK AND CONCLUSIONS

Phase Behavior and the Search for Isopycnic Phases

Ternary mixtures of a nonionic C_iE_j surfactant, CO_2, and H_2O will form three coexisting equilibrium phases at elevated pressures and ambient or slightly higher temperatures [1]. The three phases are: (1) a H_2O-rich liquid phase, (2) a CO_2-rich gas phase, and (3) a fluid phase with properties that can be varied between those of the other two phases depending on the pressure. In previous experimental work on the phase diagram for mixtures of C_8E_3, CO_2, and H_2O [1], we determined that the densities of the H_2O-rich liquid phase and the third fluid phase would approach one another with increasing pressure. We have extended those observations in the present work to predict the temperature and pressure at which isopycnic phases will form using a modified Peng-Robinson equation of state [2]. Equation-of-state parameters were regressed from data available in the literature and from our measurements of vapor-liquid equilibrium for binary mixtures of C_8E_3 and H_2O at elevated pressures and temperatures of 40 and 50°C. The calculated results are shown in Figure 1 as a plot of phase densities for the water-rich liquid phase (L1 in this figure) and the surfactant-rich, third fluid phase (L2 in this figure) as a function of pressure at 40°C. As expected, the density of the L1 phase is much less sensitive to pressure than the L2 phase, and the density of the L2 phase increases with pressure as this phase becomes more "liquid-like" at higher pressures and therefore can dissolve larger amounts of water and surfactant. These phase densities converge at an isopycnic point at a pressure of approximately 400 bar. As a result of these calculations, we conducted experiments to search for isopycnic phases for mixtures of C_8E_3 and C_8E_5 with CO_2 and H_2O at temperatures near 40°C and pressures up to 400 bar.

A high-pressure sapphire view cell (Insaco Inc.) was constructed based on an earlier design [1]. The cell is thermostated to ± .001 °C in a Hart Scientific high precision bath, and the temperature inside the cell was monitored with a platinum resistance thermometer (Newport Electronics). Pressure was measured with a precision Heise gauge. Slow demixing rates and wetting phenomena provide qualitative indications of near-isopycnic phase separation. However, a quantitative determination of isopycnic phases can be made from the observation of a phase inversion in which the high density, water-rich phase at the bottom of the cell inverts with the middle liquid phase. Isopycnic phase compositions can be measured with reasonable accuracy using a stoichiometric technique which does not require sampling of the phases [3]. Accurate quantitative measurements of isopycnic phase densities are made using an Anton-Paar densimeter.

A phase inversion was observed for mixtures of C_8E_5, CO_2, and H_2O at a temperature of $31.89 \pm .01°C$ and a pressure of 396 ± 10 bar. Wetting phenomena observed for other isopycnic systems -- such as the formation of large spherical droplets and a faint, wavy meniscus separating the two isopycnic phases [4] -- were also observed in the vicinity of the phase inversion for this mixture. A more accurate determination of the pressure and measurements of isopycnic phase densities using the Anton-Paar densimeter are now in progress. The formation of isopycnic phases for this mixture at reasonably moderate pressures is a result of two conditions: (1) the density of the pure surfactant is sufficiently high (.985 g/cc at 20°C) that the third fluid phase, which is surfactant-rich, has a density close to that of the water-rich liquid phase at ambient pressures; (2) the H_2O/C_8E_5 mixture critical temperature (61°C [5]) is high enough compared to the temperature of interest that the surfactant-rich fluid phase has a large water content. These conditions are expected to hold for other C_iE_j surfactants when $i > 8$ and $j > 5$, and we have begun to search for the isopycnic state points of these amphiphiles in mixtures with H_2O and CO_2.

Neutron Scattering

A sapphire neutron scattering cell (Insaco Inc.) was constructed to enable scattering experiments to be done at pressures up to 550 bar and at scattering angles of 30°. The temperature inside the cell was monitored with a platinum resistance thermometer (Newport Electronics) and maintained with an aluminum water jacket to ± 0.1 °C. Samples for neutron scattering were equilibrated in the sapphire view cell [1] before they were transferred to the scattering cell.

SANS measurements were made on mixtures of $C_{12}E_6$, CO_2, and D_2O in the water-rich one phase region (7.5 wt % surfactant on a CO_2 free basis) in solutions of varying CO_2 content of up to 4 wt %.. Representative data are shown in Figures 2 and 3 as plots of the neutron scattered intensity (on an absolute scale) as a function of q. The striking feature of the scattering curves is their upturn with decreasing q. This feature is usually attributed either to the presence of attractive interactions between colloidal-scale objects, the $C_{12}E_6$ micelles in this case, or to critical scattering. In either case, the rate of increase of the spectra measured at constant pressure (Figure 3) increases with increasing temperature rather steadily on approach to the critical temperature of CO_2 (31°C). On the other hand, at a constant temperature of 31°C, the spectra change substantially from 62 to 76 bar (the critical pressure of CO_2 is 74 bar), but do not vary significantly with a further increase in pressure to 90 bar (Figure 2). The role of attractive interactions can be more fully investigated using established methods that relate inter-aggregate interaction potentials to the scattering spectra [6].

The presence of aggregates in the solution is supported by the shape of the scattering curves measured at larger values of q (not shown). These data suggest that $C_{12}E_6$ micelles roughly 30 Å in size exist even in the presence of 4 wt % CO_2.

ACKNOWLEDGEMENTS

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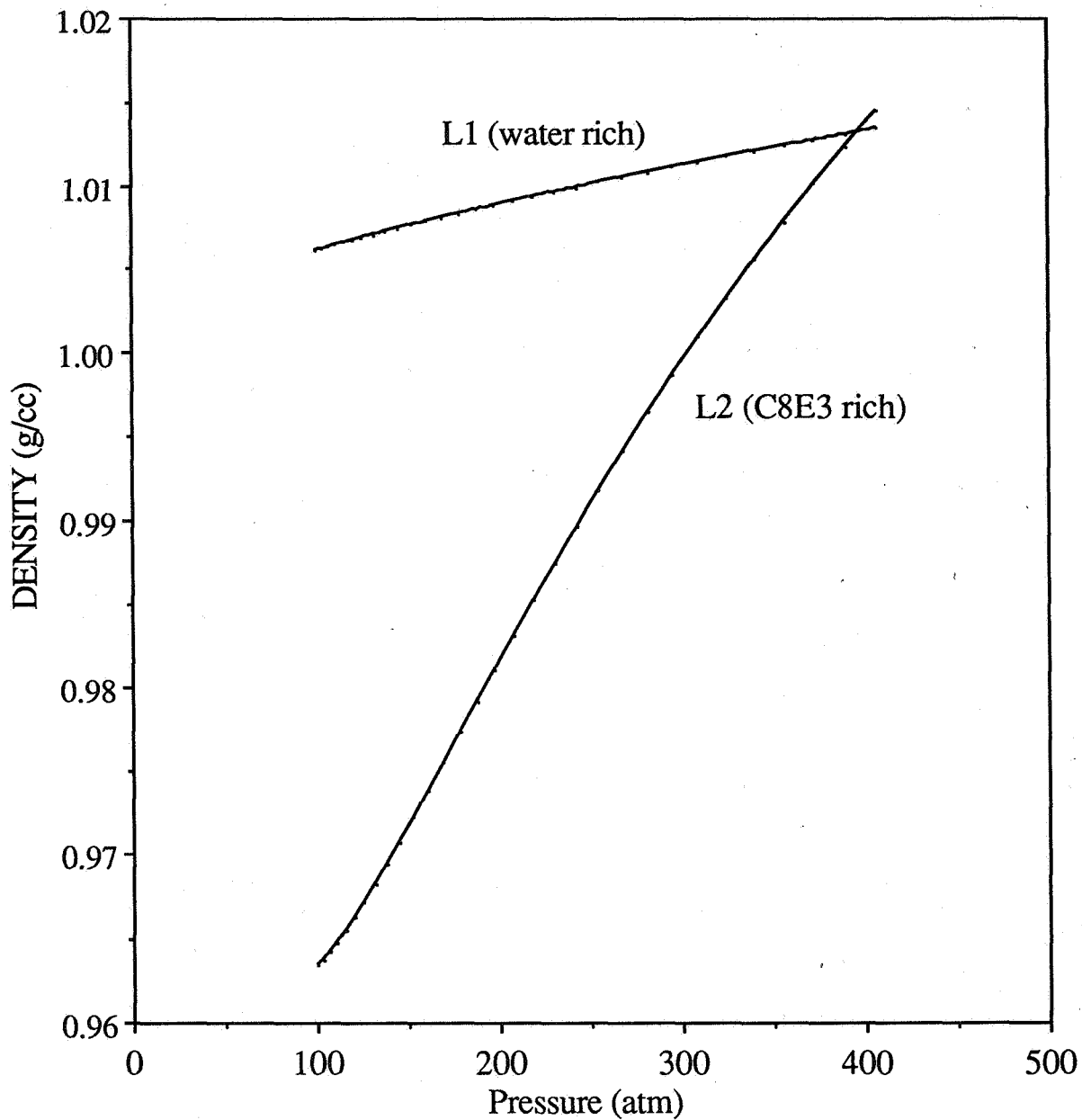
Figure 1. Calculated Phase densities as a function of pressure for the water-rich L1 liquid phase and the surfactant-rich L2 liquid phase in the presence of a CO_2-rich gas phase at 40°C for the $C_8E_3/H_2O/CO_2$ system.
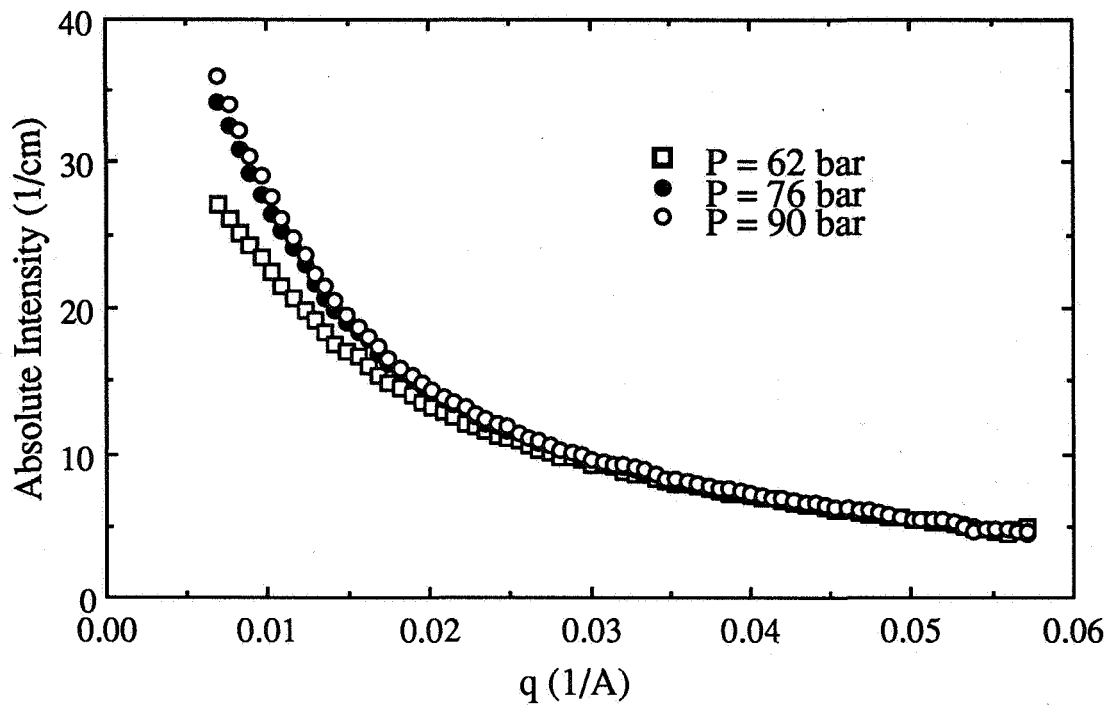
Figure 2. SANS spectra on absolute scale for a sample of 8 wt% $C_{12}E_6$, 4 wt% CO_2, and D_2O at 31°C as a function of the scattering vector q and pressure.
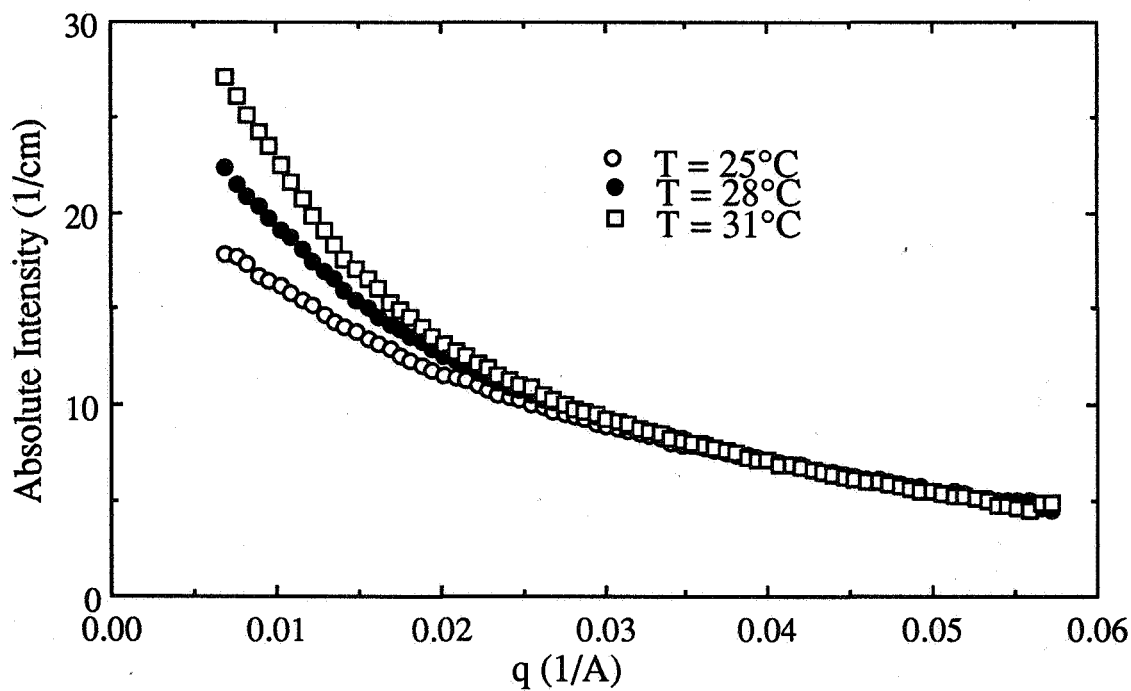

Figure 3. SANS spectra on absolute scale for a sample of 8 wt% $C_{12}E_6$, 4 wt% CO_2, and D_2O at a pressure of 62 bar as a function of the scattering vector q and temperature.