

PHASE SEPARATION KINETICS IN ISOPYCNIC MIXTURES OF H₂O/CO₂/ETHOXYLATED ALCOHOL SURFACTANTS

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Abstract

Ternary mixtures of H₂O and CO₂ with ethoxylated alcohol (C_iE_j) surfactants form three coexisting liquid phases at conditions where two of the phases have equal densities (isopycnic phases). Isopycnic phase behavior has been observed for mixtures containing C₈E₅, C₁₀E₆, and C₁₂E₆ surfactants, but not for those mixtures containing either C₄E₁ or C₈E₃ surfactants. Pressure-temperature (PT) projections for this three-phase equilibrium were determined for H₂O/CO₂/C₈E₅ and H₂O/CO₂/C₁₀E₆ mixtures at temperatures from approximately 25 to 33 °C and pressures between 90 and 350 bar. Measurements of the microstructure in H₂O/CO₂/C₁₂E₆ mixtures as a function of temperature (25-31 °C), pressure (63.1-90.7 bar), and CO₂ composition (0-3.9 wt%) have also been carried out to show that while micellar structure remains essentially unchanged, critical concentration fluctuations increase as the phase boundary and plait point are approached. In this report, we present our first measurements of the kinetics of isopycnic phase separation for ternary mixtures of H₂O/CO₂/C₈E₅.

Introduction

Surfactant solutions containing near-critical or supercritical fluids that form equilibrium phases of equal density (isopycnic phases) are uniquely suited for simulating phase separation in microgravity environments where density differences between the separating phases are irrelevant. For compressible supercritical-fluid mixtures, pressure becomes an additional operating field variable with which to adjust and control phase boundaries.¹⁻³ As a consequence, rapid pressure quenches can be made to access metastable or unstable regions of the phase diagram, thereby permitting the convenient study of phase separation dynamics and mechanisms. In addition, low interfacial tensions and the presence of colloidal microstructure in surfactant-containing solutions,^{1,3,5} retard phase separation. A goal of this work is to study isopycnic phase behavior for three-phase, liquid-liquid-liquid (L1-L2-L3) equilibrium in ternary mixtures of H₂O and CO₂ with ethoxylated alcohol (C_iE_j) surfactants: C₄E₁, C₈E₃, C₈E₅, C₁₀E₆, and C₁₂E₆. CO₂ was selected as the near-critical or supercritical fluid because it has a readily accessible critical point (31.06 °C and 73.825 bar) and a reasonably high critical density (0.4660 g/cm³).⁶

Surfactant self-assembly in near-critical or supercritical fluids opens the possibility that pressure or fluid density can be used to alter surfactant microstructure.^{7,8} Prior studies of surfactant microstructure

in solutions containing supercritical or near-critical fluids have focused on the supercritical fluid-rich region of the phase diagram where the effects of pressure on microstructure and phase behavior are expected to be large. A second goal of our work is to examine, using small angle neutron scattering, the effects of CO₂ on the interactions, critical fluctuations, and structure of ethoxylated alcohol/water micellar solutions in the water-rich region of the phase diagram. In preliminary experiments on D₂O/CO₂/C₁₂E₆ micellar solutions,⁹ we found that the scattering spectra can be modeled using a polydisperse hard-sphere form factor to determine particle shape and size, together with an Ornstein-Zernike structure factor to quantify the critical phenomena. Our results indicate the presence of spherical micelles approximately 50 Å in diameter. Further, micelle structure does not change over the range of temperatures, pressures, and compositions studied. The increase in S(0) and ξ are consistent with increasing critical concentration fluctuations caused by the approach to the phase boundary and a plait point.

Little is known about the rate of formation and growth of new phases. A third goal of this work is to investigate the separation of an equilibrium phase into two phases after both pressure and temperature quenches. Since isopycnic surfactant solutions have intrinsically slower times for mass transfer compared to molecular solutions, temperature changes and pressure changes that equilibrate within less than a few minutes are expected to be essentially instantaneous on the time scale of the phase separation kinetics. Limited observations have been made of isopycnic phase separation.^{10,11} From this previous work,¹¹ we anticipate observations of dissipative structures as the density difference between the phases vanishes. Elimination of convection driven by buoyancy will enable easier analysis of quasilastic light scattering data. The important role of viscosity in controlling the evolution of these phases can also be determined. Our combined small angle light and neutron scattering observations of the growth of new phases on length scales ranging from 10 Å to 10 μm or more will provide a unique base of information to guide and test emerging theories. This information will also be central to the exploitation of the microgravity environment of space to mitigate density differences in producing new alloys or other materials. In this report, we present our first measurements of the kinetics of isopycnic phase separation for ternary mixtures of H₂O/CO₂/C₈E₅.

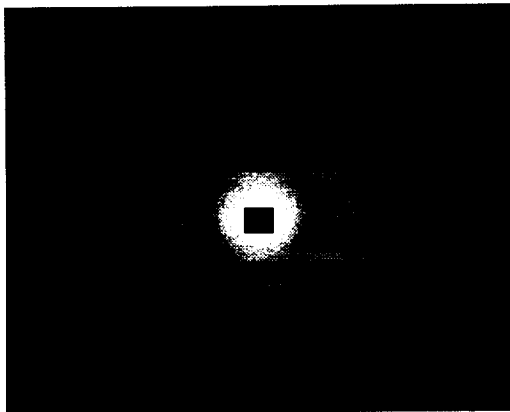


Fig. 1 Pattern of scattered light after a quench from a one-phase into a two-phase region: spinodal ring. The square in the center is a beamstop that protects the camera from the transmitted beam.

Experimental Section

Pentaethylene glycol monoethyl ether (C_8E_5) (Bachem Bioscience Inc.) with a purity of 97 wt-% and research grade CO_2 (> 99.998 %, Potomac Airgas, Inc.) were used without further purification. H_2O was filtered and purified using a Millipore apparatus.

Phase separation kinetics in ternary mixtures of $H_2O/CO_2/C_8E_5$ are measured by means of time resolved small angle light scattering (SALS). The experimental setup consists of the sapphire view cell used in our phase equilibrium studies⁹ and a scattering cell, designed and constructed in-house. The scattering cell has two 5 mm thick sapphire windows, placed parallel to each other and separated by a distance of 1 mm. The windows are sealed against the stainless steel body of the scattering cell by custom-made Teflon seals. The scattering cell and view cell are connected to each other through high-pressure tubing to enable the scattering cell to be filled from the view cell and to pressurize the contents of the scattering cell using the pressurizing system for the view cell. The system pressure is measured to an accuracy of 0.1 % using an Omega PX 945 pressure transducer. A Teflon coated stir bar in the scattering cell allows mixing using an external magnet. The scattering cell has been tested up to a pressure of approximately 500 bar. Temperature is controlled by placing the scattering cell in an aluminum jacket through which water from a Hart Scientific high precision bath is circulated. The view cell is immersed in this bath. The scattering cell temperature is measured by a thermistor located in the aluminum jacket. Pressure quenches from the one-phase region into the two-phase, L1-L2 region of the phase diagram are accomplished by instantaneously decreasing the pressure in the view cell. Thus, time resolved scattering data can be collected using the scattering cell, while simultaneously monitoring the

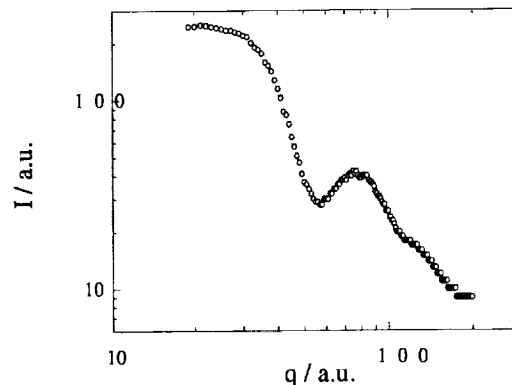


Fig. 2 Radially integrated intensity of the scattering pattern shown in Fig. 1. The relative maximum corresponds to a wave vector of $2.1 \times 10^3 \text{ nm}^{-1}$.

phase behavior of the system at identical conditions in the view cell.

The optical system consists of a He-Ne laser ($\lambda = 632.8 \text{ nm}$) that is focused to a point in the sample volume using a lens with 30 cm focal length. The scattered light is captured on a mica screen at a distance of 50 cm from the sample. The resulting scattering pattern is recorded by a CCD camera (Cohu 4910) connected to a frame grabber card (Scion LG-3) in a Macintosh G3 computer using Scion software. With this setup, up to 30 scattering patterns can be recorded per second. The data are processed using NIH Image software and data reduction software comparable to the modules used by NIST for analysis of SANS data. We plot the scattering intensity as function of the absolute of the scattering vector, q , given by

$$q = (4\pi/\lambda) \sin(\theta/2)$$

where q is the scattering angle and λ is the wavelength of the He-Ne laser.

Results and Discussion

Isothermal pressure quenches from the one-phase into the two-phase region, where surfactant-rich and surfactant-lean phases coexist (the L1 and L2 phases, respectively) were performed. Ideally, the final pressure after the quench brings the system to isopycnic L1 and L2 phases. While these phases separate, a spinodal ring is observed in the light scattering pattern, as shown in Fig. 1. This spinodal ring corresponds to a relative maximum in the plot of scattering intensity vs. q . An example of such a plot is given in Fig. 2 for a measurement after a pressure quench into the two-phase region of approximately 5 bar. The observed maximum corresponds to $q = 2.1 \times 10^3 \text{ nm}^{-1}$, which indicates the existence of scattering entities having an approximate length scale of 470 nm. However, a large scattered intensity is also found for very small q val-

ues. Therefore, we assume that even larger structures are present in the solution. We note that the apparent saturation in scattering intensity for $q \rightarrow 0$ is an experimental artifact. In order to resolve the local maximum in the spectrum, the CCD camera gain had to be increased causing the apparent saturation at very small scattering angles.

This local maximum moves to smaller values of q with time between when it is first observed 2.5 minutes after the pressure quench and completely vanishes approximately 45.0 minutes later. At longer times, light is merely scattered to very small scattering angles; i.e., large droplets or clusters of the second phase have formed. Thus, the observed spinodal ring decreases in diameter over time revealing, as expected, so-called coarsening: the length scale characterizing the domains formed immediately after the pressure quench into the two phase region increases over time.

Conclusions

The data collected so far show that isothermal pressure quenches from a one-phase region into the two-phase region corresponding approximately to isopycnic L1 and L2 equilibrium phases result in patterns of the scattered light (spinodal rings) typical of early phase separation. The time evolution of these scattering patterns show the expected coarsening of the non-equilibrium structures over time. We are currently focusing on the kinetics of this coarsening to obtain quantitative measurements of the phase separation kinetics.

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References

1. J. M. Ritter and M. E. Paulaitis, *Langmuir* **6**, 934-941 (1990).
2. G. J. McFann and K. P. Johnston, *Langmuir* **9**, 2942-2948 (1993).
3. G. J. McFann, K. P. Johnston, and S. M. Howdle, *AIChE J.* **40**, 543-555 (1994).
4. E. W. Kaler, J. F. Billman, J. L. Fulton and R. D. Smith, *J. Phys. Chem.* **95**, 458-462 (1991).
5. J. M. Tingey, J. L. Fulton, D. W. Matson and R. D. Smith, *J. Phys. Chem.* **95**, 1443-1448 (1991).
6. "Carbon Dioxide International Thermodynamic Properties of the Fluid State -3;" S. Angus, B. Armstrong and K. M. d. Reuk, Eds.; Pergamon Press: Oxford, 1976.
7. J. L. Fulton and R. D. Smith, *J. Phys. Chem.* **92**, 2903-2907 (1988).
8. R. W. Gale, J. L. Fulton and R. D. Smith, *J. Am. Chem. Soc.* **109**, 920-921 (1987).
9. R. G. Zielinski, E. W. Kaler and M. E. Paulaitis, *J. Phys. Chem.* **99**, 10354-10358 (1995).
10. C. Houessou, P. Guenoun, R. Gastaud, F. Perrot and D. Beysens, *Phys. Rev. A* **32**, 1818-1821 (1985).
11. G. M. Schneider, M. Dittman, U. Metz and J. Wenzel, *J. Pure & Applied Chem.* **59**, 79-86 (1987).