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of problems involving waste disposal, decontamination technologies, solute extractions and chemical reaction processes. This program has involved two related major activities: (1) exploration of selected ternary and quaternary systems composed of surfactant (and, possibly, a co-surfactant), water and supercritical fluids to characterize their physicochemical properties using analytical methods such as conductivity, quasi-elastic light scattering (QLS) and the UV-visible and FTIR spectroscopy of probe molecules within the microemulsion; and (2) study of the properties of microemulsions formed in supercritical fluids relevant to the enhancement of extraction and reaction rates.

FINAL REPORT

FUNDAMENTAL INVESTIGATION OF MICELLES AND MICROEMULSIONS IN SUPERCRITICAL
FLUIDS

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I. STATEMENT OF PROBLEM

Exploratory research at Battelle-Northwest during 1985-1986 led to the discovery of the existence of microemulsion phases in supercritical fluids. These results initiated a three year study funded by ARO to characterize the potentially important properties of these systems.

Microemulsions are clear, thermodynamically stable solutions generally containing water, a surfactant, and an oil (i.e., a nonpolar or low polarity fluid). The surfactant molecules form organized molecular aggregates and preferentially occupy the interface between the oil and water phases. The oil and water microdomains have characteristic structural dimensions between 2 and 100 nm. Aggregates of this size are poor scatterers of visible light and hence these solutions are optically clear. Water-in-oil (w/o) microemulsions (which are predominantly oil) and oil-in-water (o/w) microemulsion (which are typically mostly water) can have a multitude of different microscopic structures; sphere, rod, or disc shaped structures and layered or bicontinuous structures are commonly attributed to specific systems.

The combination of the unique properties of supercritical fluids (e.g., low viscosity, high-diffusion rates, variable solvent properties, etc.) with those of a dispersed microemulsion (or reverse micelle) phase creates a whole new class of solvents. The microemulsion phase adds to the properties of the supercritical fluid what amounts to a second solvent environment, which is highly polar and which may be manipulated using pressure. This second phase can itself manifest a wide range of solvent properties. Although supercritical fluids are very attractive for separation and reaction processes, owing to their density dependent properties, they are limited at moderate temperatures and pressure by their inability to appreciably solvate most moderately polar solutes and nearly all ionic materials. The addition of a dispersed stable droplet phase (forming a microemulsion) provides a convenient means of solubilizing highly polar or ionic species into the low polarity environment of the supercritical fluid phase. Hence the combination of supercritical solvents with microemulsion structures provides a new type of solvent with some unusual and important properties of potential interest to a range of technologies.

The goal of this 3-year program has been to characterize the physicochemical properties of microemulsions formed in supercritical fluids so as to determine their potential relevance to applications of Army laboratories. Included in this program has been an investigation of extraction and reaction processes utilizing microemulsions formed in supercritical fluids. Supercritical fluid microemulsions may ultimately be applied to a range

of problems involving waste disposal, decontamination technologies, solute extractions and chemical reaction processes. This program has involved two related major activities: (1) exploration of selected ternary and quaternary systems composed of surfactant (and, possibly, a co-surfactant), water and supercritical fluids to characterize their physicochemical properties using analytical methods such as conductivity, quasi-elastic light scattering (QLS) and the UV-visible and FTIR spectroscopy of probe molecules within the microemulsion; and (2) study of the properties of microemulsions formed in supercritical fluids relevant to the enhancement of extraction and reaction rates.

II. SUMMARY OF RESULTS

Work during the three years of this project has resulted in 11 publications in four different journals, two chapters in two different symposium series and one U.S. patent. A list of all publications and the patent are given in Sections III and IV of this report. Highlights of important results obtained during the four years of this study will be given in this section. For further details on these and other results the reader is referred to the relevant publications.

Supercritical Fluid Microemulsion Characterization

Three new surfactant systems have been identified and the microstructure of each system has been determined. The systems are based upon the following components: (1) polyethylene glycol dodecyl ethers($C_{12}EO_{3-6}$)/water/supercritical propane and ethane, (2) didodecyldimethylammonium bromide (DDAB)/water/supercritical propane and (3) tergitol/water/supercritical propylene. These systems have potential practical utility and are also of interest from a fundamental viewpoint.

Regarding the structure of surfactant aggregates in supercritical fluids, the general conclusions of this study are that most of the structures known to exist in liquid microemulsion systems can be formed in supercritical fluids with one important difference. With supercritical fluids, the variation of the fluid density with pressure imparts some unusual and potentially beneficial effects to the system. The following structures have been identified in supercritical fluid microemulsion systems; (i) a water-in-oil microemulsion containing nanometer-sized droplets of water encapsulated by surfactant, (ii) a bicontinuous microemulsion with a sponge-like network of water and oil on a nanometer size scale. Preliminary results have also been obtained for a unique fluid-and-water microemulsion systems (Beckman and Smith, J. Phys. Chem., submitted). The microstructure and solvent properties of these systems have been determined using spectroscopic techniques such as light scattering (DLS), Fourier transform infrared spectroscopy (FT-IR), UV-vis spectroscopy, and conductivity measurements.

Variation of the density of the fluid phase changes the properties of the aggregate phase. For supercritical fluids, the low viscosity and high diffusivity of solutes give these systems excellent mass transport properties. Measurement of microemulsion droplet diffusion rates in fluids by light scattering have shown them to be 5-10 times higher than in conventional liquid microemulsions. Variation of the fluid density changes the strength of the attractive interaction

between the droplets. As the fluid density is reduced the magnitude of the attractive interaction increases leading to a clustering of the microemulsion droplets. These microscopic effects can manifest themselves as changes in the reaction or extraction rates due to slowing of the diffusion rate of the cluster or by changing the mechanism of exchange between the droplets in the cluster.

A particularly intriguing system is the DDAB/ water/ supercritical propane system. Variation of the amount of surfactant or the water-to-surfactant ratio induces a structural change from spherical, to rod, and finally to a bicontinuous structure. What is striking about this system is that moderate changes in the fluid density or pressure can also be used to change the microstructure. The electrical conductivity of this system changes by almost three orders of magnitude with small changes in pressure indicating a structural change from bicontinuous to micellar. This system has interesting potential uses for reactions or electrochemical processes.

For all systems studied, the stability of the microemulsion is critically dependent upon the density of the supercritical fluid phase. At relatively low densities the microemulsion is destroyed and a second, surfactant and water enriched phase forms on the bottom of the pressure vessel. This property is particularly attractive for separations and reactions requiring high recovery efficiency of the products.

Extraction and Reaction Processes In Supercritical Fluids Microemulsions

This research has shown that a wide range of highly polar, high molecular weight solutes can be dissolved in the aqueous domain of a microemulsion formed in supercritical fluids. A major limitation to the use of supercritical fluids for reaction and extraction processes has been their inability to solvate polar solutes. This limitation has been essentially overcome with the formation of a microemulsion phase in the fluid. High molecular weight proteins are soluble in supercritical fluid microemulsions and they can be extracted with high efficiency from aqueous phase. Catalysts, which are generally so polar that they are completely insoluble in supercritical fluids, can be dispersed in the microemulsions phase where they catalyze reactions in the droplet core or the surfactant interfacial region. This area of research, of tremendous potential importance, will be the subject of a "follow-on" proposal.

Relevance to Waste Recovery and Decontamination

From the results of this study it will be possible to identify specific waste recovery or decontamination problems which can be addressed using supercritical fluid systems. From a perspective of waste recovery and particularly for extraction of waste from porous solid matrixes such as soils, the mass transport properties of supercritical fluids are very attractive. The solute polarity limitation of supercritical fluids has been overcome with the incorporation of a microemulsion phase so that with proper selection of the surfactant/fluid system a more specific hazardous waste containing component can be targeted. The ability to destroy the microemulsion phase with a small change in the system pressure to recover the solute is also particularly attractive for this application. The feasibility of using microemulsion/supercritical fluid systems for waste recovery must be assessed on a case by case basis and further laboratory experiments will be required prior to full-scale application of this technique.

Microemulsions formed in supercritical fluids also have potential benefits for decontamination. A polar catalytic agent can be readily dispersed in aqueous microdomains formed in the supercritical fluid phase. In addition to the benefits derived from the excellent mass transport properties of these systems, they also have the potential of greatly increasing reaction rates for those reactions which are diffusion limited. These systems are particularly well suited for reactions involving molecular oxygen or hydrogen since both of these fluids are readily soluble in the continuous phase-supercritical fluid.

Due to their recent discovery the present utilization of this new class of microemulsion systems is non-existent. However as the beneficial properties of these systems become better known, we can safely predict that uniquely attractive applications will evolve in both the analytical and large scale process areas.

III. LIST OF PULICATIONS

Beckman, E. J., Fulton, J. L., Matson, D. W., Smith, R. D., Inverse Emulsion Polymerization of Acrylamide in Near-critical and Supercritical Continuous Phases, in *Supercritical Fluid Technology*, Johnston, K. P. and Penninger, J. L., Eds., ACS Symp. Ser. 406, 1989,184.

Beckman, E. J., Smith, R. D., Phase Behavior of Inverse Microemulsions for the Polymerization of Acrylamide in Near-critical and Supercritical Continuous Phases, *J. Phys. Chem.*, 1990,94, 345.

Blitz, J. P., Fulton, J. L., Smith, R. D., Near- and Mid-Infrared Transmission Cells for the Study of Reverse Micelle Phases in Supercritical Fluids. *Applied Spectroscopy*, 1989, 43, 812-815.

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Matson, D. W., Smith, R. D. Supercritical Fluid Technologies to Ceramic-Processing Applications. *J. Am. Ceram. Soc.* 1989, 72, 871-881.

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Tingey, J. M., Fulton, J. L. Matson, D. W. Smith, R. D. Micellar and Bicontinuous Microemulsions Formed in Both Near-Critical and Supercritical Propane, Using Didodecyldimethylammonium Bromide (DDAB) and Water, *J. Phys. Chem.* In press.

Consani, K. A., Smith, R. D. Observations on the Solubility of Surfactants and Related Molecules in Carbon Dioxide at 50 Degrees Centigrade. *J. Supercritical Fluids* 1990, 3, 51-65.

Beckman, E.J., Smith, R.D., The Effect of Pressure on a Propylene/Water/Surfactant Mixture." *J. Phys. Chem.* Submitted.

Beckman, E.J., Smith, R.D., Microemulsion Polymerization within Near-critical and Supercritical Continuous Phases: Effect of Microemulsion Structure on the Reaction Characteristics." J. Supercritical Fluids. In press.

Yee, G. G, Fulton, J. L., Smith, R. D. "Study of the Partitioning of Sodium Bis(2-ethylhexyl) Sulfosuccinate(AOT) between Water and Near-critical Propane by Infrared Spectroscopy." J. Phys. Chem. In press

IV. PATENTS

United States Patent Number 4,933,404; Issued June 12, 1990; Titled "Process for Microemulsion Polymerization Employing Novel Microemulsion Systems" Inventors, Eric J. Beckman, Richard D. Smith, John L. Fulton.

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