Organized Molecular Assemblies in the Gas Phase: Reverse Micelles and Microemulsions in Supercritical Fluids

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Micelles and microemulsions are transparent solutions of thermodynamically stable organized molecular assemblies which have tremendous importance. Reverse (or inverse) micelles consist, in the simplest case, of a bulk liquid phase of low polarity, a surfactant, and usually water (which is contained in the micelle core).[1-3] Reverse micelles are attracting attention for a wide range of applications which include separations, chromatography, and reaction processes that exploit the unique combination of solvent properties.[1,4,5] In this paper we report the first observations of reverse micelles in supercritical fluid (dense gas) solvents.

Our initial studies have explored reverse micelles using the surfactant sodium bis(2-ethylhexyl) sulfosuccinate or Aerosol-OT (AOT) with various supercritical fluids as the continuous phase. Supercritical fluids provide variable properties which extend from the gas to near-liquid phase limits and which can be readily manipulated by pressure or temperature. The variable solvent properties include viscosities and diffusion rates (also dependent upon fluid density) which are intermediate between the gas- and liquid-phase values.[6,7] Supercritical reverse-micellar solutions combine the high diffusivities and variable (organophilic) solvating power of the supercritical fluid with the (hydrophilic) solvating ability of the reverse micelle. The transport properties of such systems are expected to be primarily governed by the fluid pressure with the micelles or microemulsions contributing what amounts to a second, suspended, highly polar phase to the solvent. Thus we anticipate that supercritical fluids would provide novel control of the solvent properties of the continuous nonpolar phase of reverse-micelle systems, providing the basis for unique studies of micelle properties and potential new applications. Micelles also extend applicability of processes based upon supercritical fluids to highly polar and labile compounds which would be otherwise impractical due to low solubility.[6,8,9]

The primary experimental method utilized to determine the presence of reverse micelles was visual observation of the solvation of highly polar, colored azo dyes (malachite green [*p*,*p*′-(*p*-phenylmethylidene)bis(*N*,*N*-dimethylaniline)] and methyl red [2-[*p*-(dimethylamino)phenyl]azo]benzoic acid] or a protein (cytochrome C) in supercritical fluid–AOT–water systems. Solubilization of malachite green and cytochrome C into liquid alkane reverse micelles has been previously reported.[4,5,10] These substances were determined to have negligible solubility in both the supercritical hydrocarbon and the supercritical hydrocarbon saturated with water in the absence of the surfactant. A number of additional supercritical fluids have been briefly examined (CF_3Cl, SF_6, CO_2, N_2O); however, AOT reverse micelles were formed at only moderate pressures in hydrocarbon solvents (e.g., ethane, propane, *n*-butane, and *n*-pentane), which our initial studies have examined in greatest detail. In addition to visual studies, solution densities as a function of temperature and pressure, were measured using a Mettler Model DMA 512 densimeter. The formation of reverse micelles was investigated as a function of temperature, pressure, and surfactant concentration, to partially define the relevant phase diagram boundaries. Extension of visual studies to supercritical pentane exceeded the thermal stability limit of AOT (~150 °C). Reverse micelles in liquid pentane were observed to this temperature at elevated pressures. To confirm the presence of micelles in supercritical pentane, a fluorescence capillary flow cell arrangement (as typically configured for chromatographic detection) was used which minimized the time at elevated temperatures.

Table I. Comparison of the Maximum W_0 for Various *n*-Alkanes

	T_c,[d] °C	P_c,[d] bar	W_0(max)
supercritical ethane[a]	32.4	34.8	1-5
supercritical propane[a]	97.0	43.3	~10
liquid propane[b]	97.0	43.3	~20
liquid pentane[b]	196	33.2	22
liquid octane[c]	296	24.5	20
liquid decane[c]	344	20.8	30

[a] Supercritical fluids investigated in this study (ethane 37 °C, 250 bar; propane 110 °C, 250 bar). [b] Liquids investigated in this study (propane 37 °C, 250 bar; pentane 25 °C, 1 bar). [c] From ref 11 and 12 (T = 25 °C, P = 1 bar). [d] Critical parameter for *n*-alkane phase.

In all the supercritical alkane systems studied, the dissolution of AOT (at low water concentrations) occurs in three stages as the fluid density increases. At low fluid densities, three phases exist: solid AOT, a viscous AOT–alkane liquid mixture, and a gaseous alkane upper phase. At intermediate densities an AOT–alkane liquid phase exists in equilibrium with a predominately gaseous alkane upper phase. Finally, at higher densities a single micelle-containing phase is formed. As water is added to this phase, the micelles are "swollen" to sizes which accept the polar dyes. As the density of this solution is slowly reduced, a sharp phase transition occurs with precipitation of a second dye-containing phase and the apparent destruction of the micelle phase.

The propane–AOT–water system at higher pressures was in many respects similar to larger liquid alkane systems. Solubility of the AOT monomer in liquid propane (at 25 °C and pressures slightly above its vapor pressure) is similar to that in typical hydrocarbon solvents (~4×10^{-4} M). A key property of reverse micelles is the water-to-AOT ratio, $W_0([H_2O]/[AOT])$, since for $W_0 < 10$ the water molecules have solvent properties influenced by interaction with the surfactant while a larger W_0 results in a water core with conventional solvent properties.[1-3,10] Table I gives the maximum W_0 values for supercritical alkane–AOT–water systems. W_0 values in liquid propane are slightly lower than those reported for *n*-octane.[11-13] Over the temperature and pressure ranges where reverse micelles are found, W_0 values in supercritical propane appear to vary significantly from those of the liquid. The minimum pressure observed for micelle formation in propane was ~120 bar at 105 °C. Reverse micelles formed in both liquid and supercritical propane were observed to solubilize large, hydrophilic molecules such as cytochrome C (MW = 13 000).

Micelle formation in supercritical ethane was markedly different than in the larger alkanes and was studied in greater detail. Addition of supercritical ethane to a surfactant–water mixture at lower pressures results initially in uptake of ethane into the condensed phase. As density is further increased, by addition of ethane, a single phase containing micelles results. At a fixed temperature (37 °C) and pressure (250 bar) the reverse-micelle

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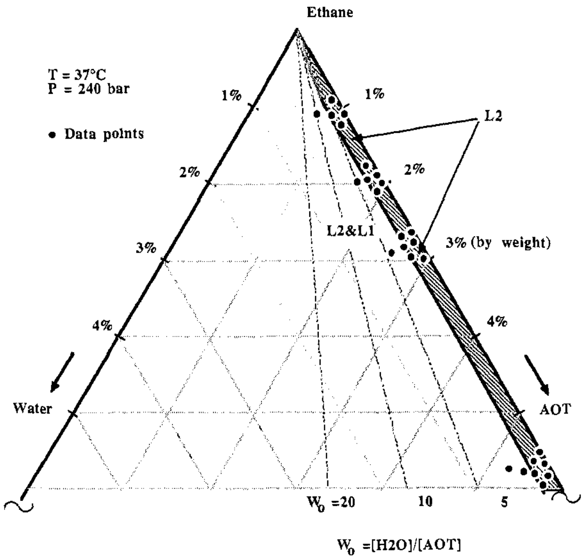

Figure 1. Ethane-rich corner of the ethane–AOT–water ternary phase diagram. L2 is the reverse micelle in supercritical ethane phase; L1 is a liquid phase which containing AOT, water, and ethane.

formation depends on the AOT and water concentration as shown in Figure 1. W_0 in supercritical ethane at these conditions exhibits behavior different from larger liquid *n*-alkane systems.[14] First, the maximum W_0 is dependent on AOT concentration; second, W_0 is much lower than for other hydrocarbon systems. The low W_0 values observed in both supercritical ethane and propane are tentatively explained in terms of the "packing ratio" model described by Mitchell and Ninham.[15,16] The area occupied by the polar head groups remains constant at fixed pH and ionic content. In contrast, the greater penetration of the surfactant tails and the larger volume solvated by the supercritical fluid result in an interfacial surfactant layer which will have higher curvature; thus only smaller micelles can exist.

As the supercritical ethane density is reduced, the single micellar phase is destroyed and two phases are formed consisting of an AOT–water-rich liquid phase and a predominantly ethane upper phase. As shown in Figure 2, the minimum ethane density for micelle stability decreases as the temperature is increased; this suggests that the increase in thermal energy is sufficient to offset the loss of ethane solvating power at the lower fluid density. The density range over which dissolution and micellization occurs differs for subcritical liquid and supercritical ethane; this can also be attributed to the temperature difference of the two phases.

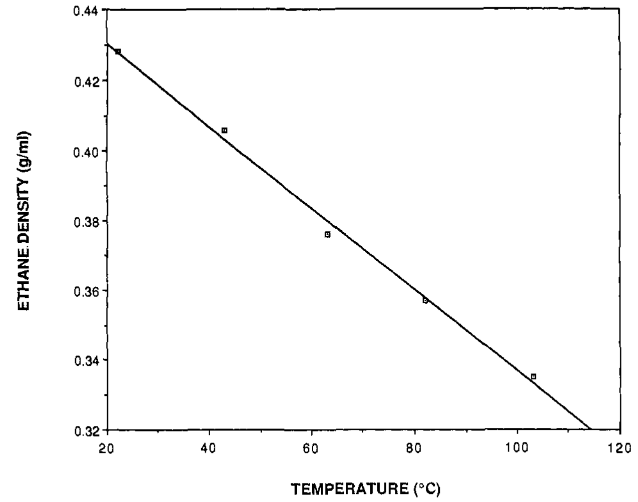

Figure 2. Minimum supercritical ethane (T_c = 32.4 °C) density required for the formation of stable reverse micelles as a function of temperature. Densities correspond closely to those for the pure ethane at similar conditions.

There are several interesting possible technological applications of supercritical fluid micelles or microemulsions. Diffusion coefficients are up to 10^2 higher in the continuous supercritical fluid phase than in liquids. Similarly, viscosity is up to 10^2 lower in such fluids. This combination of properties should allow very high mass transfer rates in extractions from liquid or porous solid phases or high overall rates for interfacial reaction processes. By changing the size or shape of the micelle by varying the fluid density, the selectivity of the micelle core in extractions or the properties of the micelle environment for chemical reactions can be changed. Also, supercritical fluid density is a much less constrained variable than temperature in controlling micellar phase behavior; in contrast to liquid systems where pressure and temperature have only moderate utility. A small decrease in density could be used to alter the phase behavior and thus "unload" the micelle contents for final product recovery after extraction. The step could be reversed by a small increase in density to rapidly reform the micelles. Equivalent control is absent in liquid systems where ionic strength or pH are typically used to manipulate phase behavior. Further studies are in progress aimed at both the investigation of reverse-micelle phase behavior and properties and the development of separation and chromatographic processes utilizing the unique solvating characteristics of both the supercritical fluids and reverse-micellar phases.

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Asymmetric Induction in Grignard and Hetero-Diels–Alder Reactions of Chiral α,β-Unsaturated Carbonyl Compounds[1]

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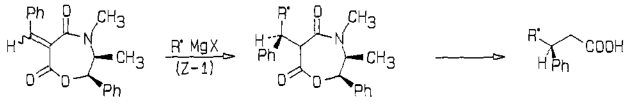
The diastereoselective addition of nucleophiles to α,β-unsaturated carbonyl derivatives is an important method in asymmetric synthesis of enantiomerically pure compounds.[2] The 6-benzylidene-oxazepane-5,7-dione **1**, which was introduced by Mukaiyama[3] is an effective chiral acceptor. Thus, the addition of Grignard reagents to **1** leads to **2** which after hydrolysis affords 3-substituted carboxylic acids **3** with high enantiomeric excess.



Z-1
E-1
2
3

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