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REVERSE MICELLE SUPERCRITICAL FLUID SEPARATIONS

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ABSTRACT

Initial results are presented showing the potential applications of reverse micelle supercritical fluid solvents in separation processes. The formation of reverse micelles in supercritical n-alkane continuous phases is described. Phase diagrams obtained from view-cell studies of micellar and microemulsion phases formed in supercritical fluids are reported and shown to be strongly dependent on pressure. The solubility of AOT in ethane and propane over a range of pressures shows behavior typical of solids in supercritical fluids. The maximum water-to-surfactant ratio (W_0) increased dramatically in both ethane and propane systems as pressure was increased. At 300 bar W_0 = 4 for ethane at 37 °C and W_0 = 12 for propane at 103 °C. The initial use of supercritical fluids containing reverse micelles for the extraction of solutes from an aqueous phase, and as mobile phases in chromatography, is described.

INTRODUCTION

The use of organized media in separation processes is becoming increasingly important. Recently, particular attention has focused on the use of reverse micelle systems. Reverse (or inverted) micelles are small, dynamic aggregates of surfactant molecules surrounding a polar (typically aqueous) core dispersed in a nonpolar continuous (oil) phase. Reverse micelle solutions are clear and thermodynamically stable; at some arbitrarily large

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(a) Operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830 water to surfactant ratio (W), which is also a measure of micelle size, the systems are preferably referred to as microemulsions. There is increasing interest in utilizing reverse micelle and microemulsion solutions for enhanced oil recovery (1,2), for the separation of proteins from aqueous solutions (3,4), as reaction media for catalytic (5) or enzymatic (6) reactions, and as mobile phases in chromatographic separations (7,8).

Studies of reverse micelle solutions to date have been at temperatures well below the critical temperature (T_c) of the continuous liquid phase. For example, the critical temperature of iso-octane, which has been widely studied for AOT reverse micelles, is 288 °C and the critical pressure (P_c) is 45 bar. At moderate temperatures the low molecular weight hydrocarbons, such as ethane (T_c = 32 °C, P_c = 48 bar) and propane (T_c = 97 °C, P_c = 42 bar), exist as supercritical fluids. For a pure component, the critical point represents the maximum temperature and pressure at which a two-phase system (liquid and vapor) can exist in equilibrium. In the supercritical fluid region, where temperature and pressure are above those at the critical point, the properties of the fluid (a dense gas) are uniquely different from either the gas or liquid states (9,10) at ambient conditions, but roughly variable with fluid pressure (or density) between the two limits. In particular, the solvating power of a supercritical fluid can be continuously varied over a wide range by adjusting fluid pressure. Additionally, the viscosities of supercritical fluids are typically 10 to 100 times lower than liquids, and diffusion coefficients are 10 to 100 times higher (10).

Recently we reported initial observations of reverse micelles and microemulsions in supercritical fluids (11). We reported that reverse micelles in supercritical alkane systems can solubilize such compounds as a highly polar dye (malachite green) and a high molecular weight protein (Cytochrome C, MW = 12,384 dalton). In this paper we describe current knowledge of the properties of reverse micelle supercritical fluid solvents. We also present results on the application of these solvent systems for extractions from an aqueous phase and as chromatographic mobile phases. The potential for broader use of this new class of solvents is briefly considered.

EXPERIMENTAL SECTION

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was obtained from Fluka (>98%, "purum") and was further purified according to the method of Kotlarchyk (12). In the final step, the purified AOT was dried in vacuo for eight hours. The molar water-to-AOT ratio, W = $[H_2O]/[AOT]$, was taken to be 1 in the purified, dried solid (12). Solutions of 50 mM AOT in iso-octane had an absorbance of less than 0.02 A.U. at 280 nm which compares favorably with AOT purified by HPLC (6). Potentiometric titration indicated that acid impurities were less than 0.2 mole % (6). The purified AOT was analyzed by mass spectrometry using 70-eV electron ionization with direct probe introduction. Two trace impurities were identified: 2-ethyl-1-hexanol and maleic acid. The ethane and propane were both "CP" grade from Linde. The iso-octane (GC-MS grade) was used as received from Burdick and Jackson. Distilled, deionized water was used throughout.

The phase behavior of the AOT/water/supercritical fluid systems was studied using a high-pressure stainless steel view cell having a 3/4 in. diameter by 3 in. cylindrical volume, capped on both ends with 1 in. diameter by 1/2 in. thick sapphire windows. Silver plated metal "C" ring seals (Helicoflex) formed the sapphire to metal seal. The fluid mixtures were agitated with a 1/2 in. long Teflon®-coated stir bar driven by a magnetic stirrer (VWR, Model 200). The insulated cell was heated electrically. Temperature was controlled to ±0.1 °C using a three-mode controller with a platinum resistance probe (Omega, No. N2001) and monitored with a platinum resistive thermometer (Fluka, No. 2180A, ±0.3 °C accuracy). The fluid pressure was measured with a bourdon-tube type pressure gauge (Heise, ± 0.3 bar accuracy). While stirring, the fluid was allowed to equilibrate thermally for 10 min. before each new reading. In selected studies, much longer observation periods (~ one day) were used to access the phase stability of these systems, although equilibria were established rapidly in the systems reported.

The procedure for finding a point on the two-phase boundary of the n-alkane/AOT/water systems was as follows. A weighed amount of solid AOT was placed in the view cell and, after flushing air from the cell with low-pressure alkane, the cell was filled to within 10 bar of the desired pressure with a high-pressure syringe pump (Varian 8500). This AOT/alkane solution was modified by injecting successive 27-µL increments of water until the two-phase boundary was reached. A hand operated syringe pump (High Pressure Equipment, No. 87-6-5) was used to slowly inject the water through a metering valve into the supercritical fluid-reverse micelle solution. By keeping the water in the syringe pump at a constant pressure slightly above the view cell pressure, the amount of injected water could be determined from the vernier scale on the screw of the pump. The same procedure was used to study phase behavior in the liquid iso-octane system.

The accuracy of the location of the phase boundary determined by the above method was verified using a slightly different technique. The weighed AOT sample was placed in the view cell, along with a predetermined amount of water, and pressurized to within 20 bar of the pressure expected to result in a single phase, and then stirred for 10 min. The fluid pressure was then increased by 10 bar by adding the alkane and then stirred again for 10 min. This procedure was repeated until a stable single-

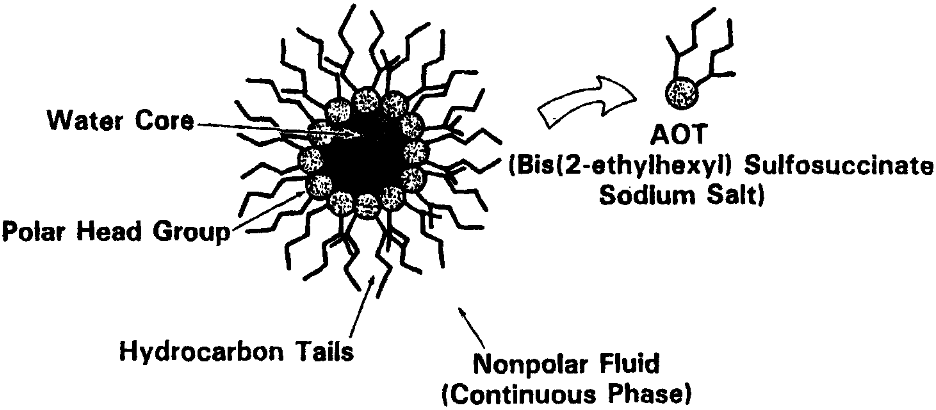

Figure 1. Idealized structure of a reverse micelle.

phase system was obtained. The phase boundaries determined for five systems were found to agree within ± 5% of the values determined from the previous measurement technique.

The solubility of "dry" AOT ($W<1$) in supercritical ethane and propane was determined by sampling an equilibrium cell using chromatographic techniques. An excess of solid AOT was loaded into a 17-mL high-pressure vessel. The fluid was saturated with AOT by recirculation through the solid bed of AOT using a magnetically coupled gear pump (Micropump, No. 182-346). The solution was sampled, by means of a HPLC valve having a 100 µL sample volume, to a UV absorbance detector (ISCO V^4) at a constant flow rate of the temperature-regulated subcritical liquid. The transport fluid (or mobile phase) was pure liquid ethane or propane at 300 bar and 25 °C. The amount of AOT in the 100-µL sample was determined by integrating the absorbance peaks (monitored at 230 nm) after calibration using solutions of known concentration and correction for differences in flow rate.

Reverse Micelles in Supercritical Fluids

The use of micellar mobile phases in liquid chromatography has recently been reviewed by Dorsey (13). An idealized structure for a reverse (or inverted) micelle is illustrated in Figure 1. Reverse micelles can be formed with certain surfactants, such as sodium bis(2-ethylhexyl) sulfosuccinate (commonly known as Aerosol-OT or AOT). Such surfactants, in contrast to normal micellar systems, typically exhibit a poorly defined critical micelle concentration (CMC).

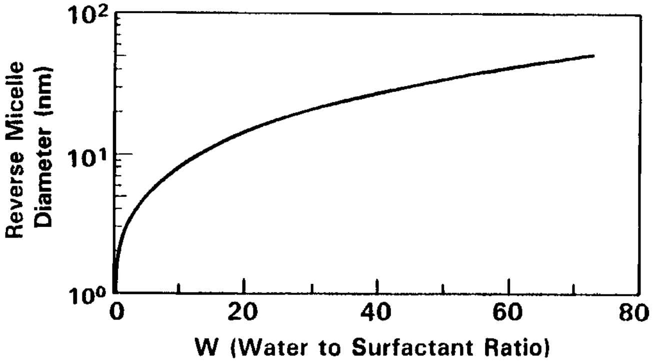

Figure 2. Calculated relationship between AOT/water reverse micelle diameter and the molar water-to-surfactant ratio (W). A maximum (W_0) is a characteristics of each reverse micelle system. Solvating properties are related to W.

For spherical reverse micelles, the molar water-to-surfactant ratio (W) can be related to the size of the micelle in a straightforward fashion, and the total interfacial area is largely determined by the amount of surfactant. Figure 2 gives micelle diameter calculated as a function of the molar ratio of water to AOT, where it is assumed that all the AOT and water is associated with the reverse micelle. In most systems a maximum water-to-surfactant ratio (W_0) exists, which can be ascribed to geometric constraints imposed by the surfactant structure and orientation and to the solvation interactions of the micelle by the continuous less polar (liquid or supercritical fluid) phase. The reverse micelles have a polar core, with solvent properties dependent upon W, which can solvate highly polar water-soluble compounds (e.g., salts, proteins and peptides) and sometimes even normally insoluble amphiliphilic compounds (6,14-16). At low W values (<8 to 10), the water in the micelle is highly structured due to association with the AOT sulfonate head groups and the surfactant counter ion. This core water may resemble an ionic fluid. At larger W values (>10 to 15), the swollen micelles (or microemulsions) have water cores which approach the solvating properties of pure water, providing a distinct third solvent environment. Large amounts of surfactant allow significant quantities of water to be solubilized in reverse micelle systems. These swollen reverse micelles (i.e., microemulsions), in turn, can solvate large amounts of polar solutes. In contrast, if water is not added to AOT/hydrocarbon systems, the reverse micelles (if formed) will usually be too small to solvate hydrophilic compounds.

TABLE I. Comparison of the Maximum Water-to-Surfactant Ratios (W_0) and Critical Propertiesfor Various n-Alkanes

	T_c (c) °C	P_c (c) bar	W_0
supercritical ethane[a]	32.4	48.2	1-5
supercritical propane[a]	97	43.3	~ 10
liquid propane[b]	97	43.3	~ 20
liquid pentane[b]	196	33.2	22
liquid octane	296	24.5	20
liquid decane	344	20.8	30

(a) Ethane 37 °C, 250 bar; propane 110 °C, 250 bar.
(b) Propane 37 °C , 250 bar; pentane 25 °C, 1 bar.
(c) Critical parameter for pure n-alkane phase.

Reverse micelles can be visualized as submicroscopic vessels providing enormous interfacial areas and solvent environments after appropriate for large or complex hydrophilic solute species. The micelles collide, coalesce, and exchange contents efficiently with other micelles (and surfaces) on a time scale of 10^{-10} to 10^{-6} seconds. Reverse micelles are typically, spherical, although other structures (e.g., spheroids and rods) can be favored under certain conditions (typically, high surfactant concentrations). Solutes partitioned into reverse micelles may be preferentially oriented relative to the micelle surface (particularly at low W), providing the potential for selectivity in their interactions.

An understanding of the phase behavior of the ternary supercritical fluid/surfactant/water systems is crucial to their application for separations. The formation of reverse micelles has been investigated for a limited range of fluids (Table I) as a function of temperature, pressure and surfactant concentration, to partially define the relevant phase boundaries. Studies to identify the presence of reverse micelles included the solvation of water-soluble dyes (insoluble in the pure fluid). The surfactant AOT has been an effective compound for forming reverse micelles in supercritical hydrocarbon solvents. It is interesting to note that reverse micelles large enough to solvate small polar dye molecules were not formed for AOT/water systems with supercritical CO_2, SF_6 or N_2O at pressures under 350 bar (8).

In the supercritical alkane systems, 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 predominantly 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 (used as probes at very low concentrations). 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 reverse micelle phase.

The propane-AOT-water system at higher pressures was in many respects similar to higher molecular weight, liquid alkane systems. Table I gives the maximum W_0 values for liquid supercritical alkane-AOT-water systems. W_0 values in liquid propane are somewhat lower than those reported for n-octane (17-19). 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 = 12,384).

The solubility of AOT in ethane as a function of ethane density is given in Figure 3 at three different temperatures. As indicated in Figure 3, there is a nearly linear relationship between log[AOT] solubility and fluid density over several orders of magnitude of AOT concentration. This type of behavior would be expected for the solubility of a non-aggregate-forming, solid substance in a supercritical fluid. The solubility and phase behavior of such solid/supercritical fluid systems can be predicted from a simple Van der Waals equation of state (10). Clearly, this approach is not appropriate for predicting surfactant solubilities in fluids, since it does not account for the formation of aggregates or their solubilization in a supercritical fluid phase.

The effect of temperature on AOT solubility in ethane is also shown in Figure 3. In our initial correspondence (11) it was shown that the minimum ethane density necessary to support reverse micelles (at $W \simeq 1$) had a nearly linear inverse relationship with temperature extending from the near-critical liquid (at 23 °C) to well into the supercritical region (>100 °C). (The previous experiments utilized an AOT concentration of $\sim 2 \times 10^{-2}$ moles/liter, and correspond to a solubility measurement in which the fluid density necessary for solvation at a given temperature is determined. The results are in good agreement with the present more extensive measurements obtained using a completely different

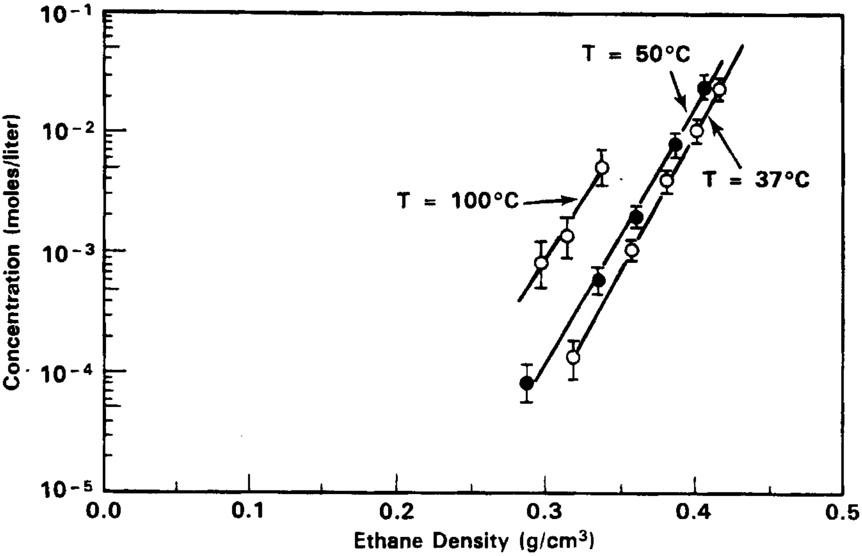

Figure 3. Solubility of AOT in supercritical ethane at 37, 50 and 100°C for W approximately equal to 1.

method.) The solubility of AOT is greater in propane than in ethane at similar temperatures, although the greater slope of the log[AOT] vs. ρ data for ethane suggests that the differences will be small at higher fluid densities.

A partial phase diagram for the supercritical propane-AOT-water ternary system at 103 °C is shown in Figure 4. Only the alkane-rich corner of the phase diagram is represented, up to a maximum of 20% water or AOT by weight. The location of the phase boundary (or W_0 when solubility of water in the hydrocarbon is neglected) for three different pressures is shown. The areas to the right of the phase boundaries are regions where a transparent single reverse micellar phase exists. To the left of the W_0 lines, a two-phase liquid-gas system exists.

The manipulation of pressure and/or W for a reverse micelle system clearly provides a method to change the solvating power of the mobile phase. Specific solvation effects involving reverse micelles in liquids have been elucidated, showing that solvation may occur in the center water pool or at the surfactant-water interface (6,14,15). Selectivity may be influenced by controlling

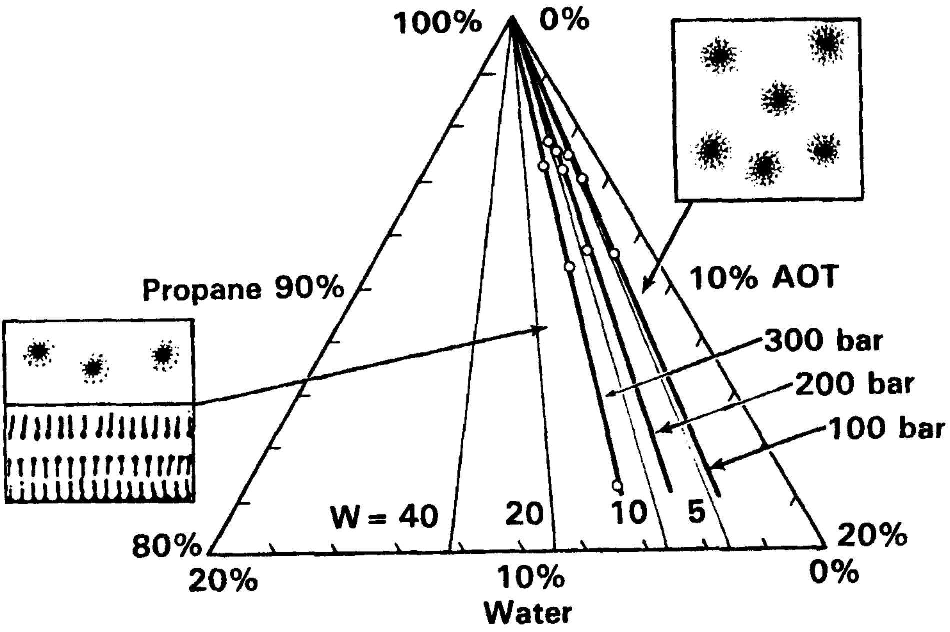

Figure 4. A portion of the ternary phase diagram for propane/AOT/water at 103°C. Lines are given which define the phase boundary between the single reverse micelle phase on right, and the two-phase system on the left, at three different pressures.

the reverse micelle structure, by varying the concentration of surfactant and water-to-surfactant ratio (W), or by adjusting the pH or ionic strength (4,6).

Reverse Micelle Supercritical Fluid Chromatography

To date, supercritical fluid chromatography (SFC) has relied on polar fluids or binary mixtures containing a polar modifier to increase the polarity of the mobile phase and to allow separation of more polar compounds (9). Relatively high critical temperatures of more polar fluids and fluid mixtures, containing substantial amounts of a polar modifier, can limit their application to labile analytes. Reactivity of some of the polar fluids (i.e., H_2O, NH_3) at supercritical conditions and related experimental complications (i.e., stationary phase stability), further hinder their use. Reverse micelle formation in supercritical solvents with low critical temperatures introduces another means of modifying the mobile phase in SFC (8,11). Supercritical mobile phases incorporating reverse micelles should offer two additional variables for controlling micelle phase behavior: temperature and pressure (or density). Reverse micelle SFC would also be anticipated to benefit from the enhanced diffusion rates and lower viscosities of such mobile phases.

Our initial investigations of reverse micelle mobile phases have explored SFC with commercially available packed columns. Preparation of the propane reverse micelle mobile phases was accomplished by addition of AOT and water to the syringe pump, filling the syringe with liquid propane, pressurizing the system to 250 bar and mixing with a small magnetically coupled pump.

Reverse micelle mobile phases for SFC can be utilized over a broad range of conditions. The fact that the water content of the micelles partially determines their solvating ability suggests that control of W_0 by pressure variation (from a two-phase system) could provide a means for manipulating the solvating power of the mobile phase. Addition of salts, polar solutes or co-surfactants can also alter W_0. Solubility in the bulk (continuous) supercritical fluid phase is also controlled by pressure, increasing the potential utility of this approach.

In our initial studies using a reverse micelle mobile phase in SFC, retention and separation efficiency were compared with a pure supercritical mobile phase and with both the pure subcritical liquid and the liquid reverse micelle mobile phases at the same temperature. Retention data for the three model compounds for the various mobile phases at 25 ° and 110 °C are given in Table II. Figure 5 shows a chromatogram obtained for the test mixture using a reverse micelle supercritical propane mobile phase with a silica (5 μm particle size) microbore column. At constant temperature, the capacity factors (k') were found to decrease substantially for all solutes when the pure solvent mobile phase was replaced with a reverse micelle mobile phase using the same solvent. Although the solvent strength of liquid propane is much less than n-hexane (k' in propane was greater than 100 for all three analytes), the reverse micelle mobile phases of both solvents gave similar retention at 25 °C. This suggests that the major effect on retention is due to the presence of the surfactant.

Solute retention (Table II) for the pure solvent mobile phases decreases at elevated temperatures, as expected (8). In the reverse micelle mobile phases, retention of phenol and 2-naphthol decreases by a small amount, and retention of resorcinol increased slightly with increasing temperature. The latter was unexpected based solely on an adsorption retention mechanism. Large changes in retention were previously reported in liquids for AOT concentrations below the critical micelle concentration (7).

Table II. Retention (k')(a) as a function of mobile phase composition and temperature Pressure 250 bar, [AOT] = 5×10^{-2} M, W = 5.0

	Hexane		Hexane/AOT/H_2O	
Temperature (°C)	25	110	25	110
phenol	62±2	4.09±0.08	4.50±0.11	1.69±0.03
2-naphthol	65±2	6.17±0.25	3.82±0.09	1.73±0.03
resorcinol	>100	>73	11.7±0.10	12.2±0.1
System(b)	Propane		Propane/AOT/H_2O	
Temperature (°C)	25	110(b)	25	110(b)
phenol	>100	4.39±0.12	2.76±0.05	1.34±0.06
2-naphthol	>100	9.09±0.23	2.34±0.12	1.60±0.12
resorcinol	>100	>100	7.99±0.10	8.45±0.05

(a) $k' = (t_r - t_o)/t_o$; ±SD, n = 3.

(b) The propane phase is supercritical and has a density of 0.48 g/ml.

It remains to be determined whether a shift in the critical micelle concentration (or W) in going from 25 to 100 °C could account for such behavior (which could be selective in the effect upon retention depending upon the location of solute partitioning).

The chromatographic efficiency with supercritical reverse micelle mobile phases offers advantages over liquid reverse micelle phases. Hernadez-Torres et al. (7) reported that efficiency decreased for liquid mobile phases which contained reverse micelles compared with non-micellar phases, and attributed this to the slow rate of solute partitioning (secondary equilibria) into and out of the micelle phase. Our results have shown that efficiency generally increases with mobile phase temperature (8). Increased efficiencies are expected by operating above the critical temperature (of the continuous phase) and at moderate fluid densities because of higher diffusion rates and lower viscosities compared with liquids; the general advantage of

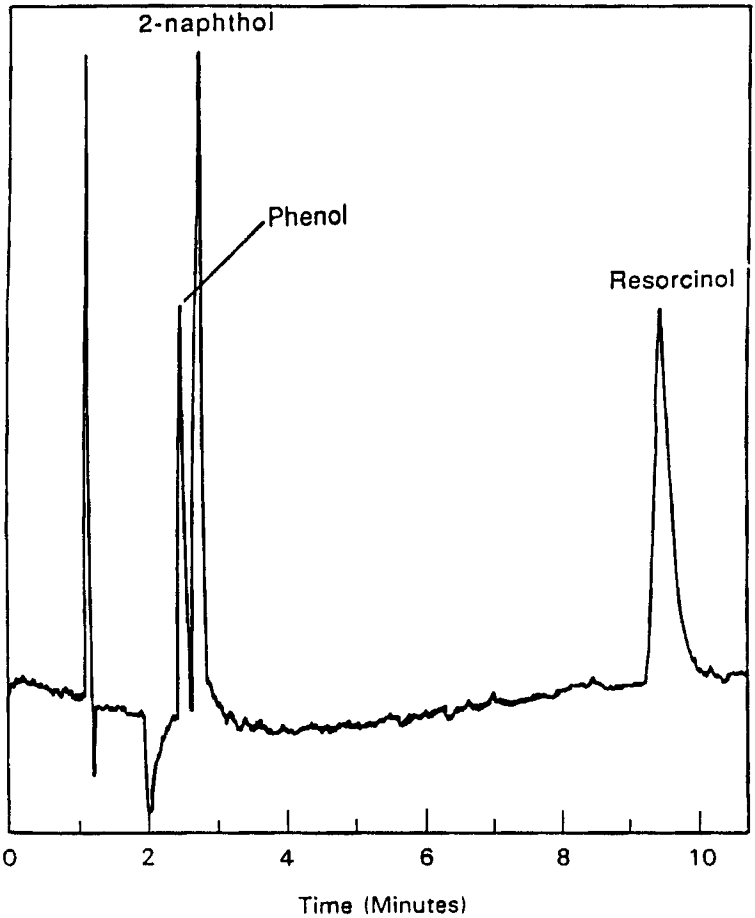

Figure 5. Reversed micelle superciritcal propane chromatogram. Propane 110°C, 250 bar. [AOT] = 5 x 10^{-2} M, W = 5.0.

supercritical fluids for SFC in comparison with liquids. One reason that reverse micelle chromatography may be better adapted to supercritical fluids is that this gain in efficiency at higher temperatures tends to minimize the loss in efficiency due to the use of micelle systems. The higher diffusion rates and lower viscosities of supercritical fluids, compared with those of liquids at the same temperature, may enhance micelle diffusion rates leading to an increased overall efficiency.

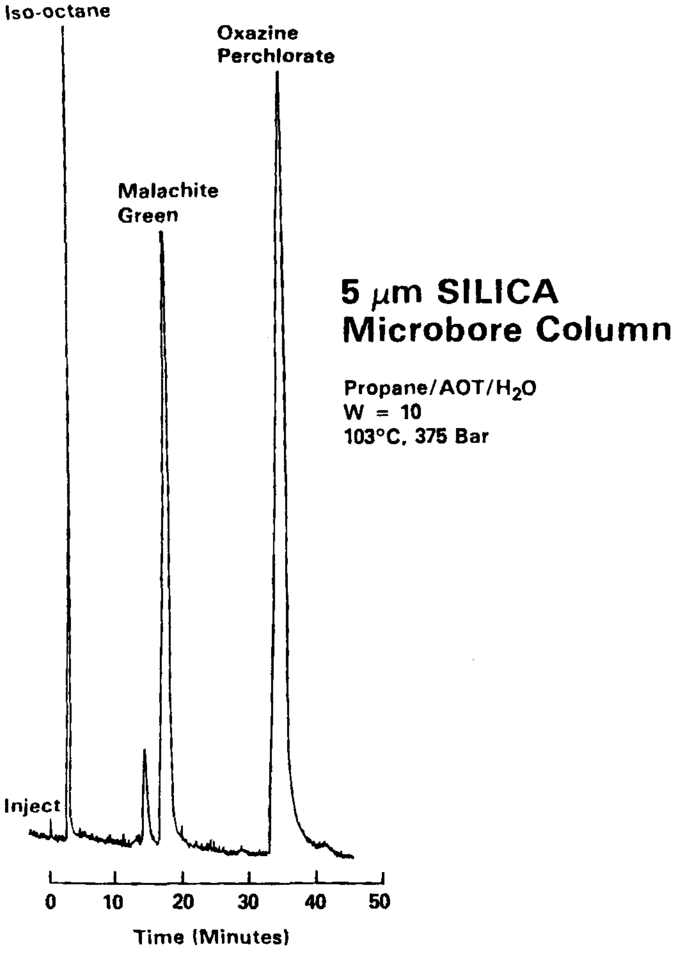

Figure 6. Reverse micelle SFC separation of two polar dyes.

While the studies discussed above provide useful insight into the nature of reverse micelle mobile phases, the value of reverse micelle SFC will depend upon its applicability to previously intractable (at least by SFC or GC) hydrophilic compounds. An example of such an application is shown in Figure 6, which shows reverse micelle supercritical fluid chromatography of a mixture containing two highly polar water-soluble dyes (malachite green and oxazine perchlorate). In this case a solution of 5 x 10^{-2} M AOT with W = 10 in propane at 103 °C and 375 bar was used as the mobile phase. The chromatographic column was the same C_{18} microbore column used for the previous studies. The sample was injected in a reverse micelle solution using liquid iso-octane as the continuous phase. The two components were also well separated form the iso-octane peak and studies at various W values showed that retention and selectivity could be varied over a wide range. To our knowledge the compounds addressed in Figure 6 could not be solvated using nonpolar liquids or conventional pure (or binary) supercritical mobile phases.

The potential exists to tremendously extend the range of applicability of SFC using reverse micelle mobile phases. Successful development of reverse micelle mobile phases for SFC will depend upon a better understanding of the complex phase behavior of these systems and obtaining chromatographic efficiencies which offer clear advantages compared to liquid chromatography. The phase behavior can change over the range of temperatures and pressures associated with the preparation and actual use of reverse micelle phases. Thus, it is important to know (at a minimum) that the mobile phase will exist as a one-phase system in the syringe pump and through the chromatographic system.

Extractions with Reverse Micelle Supercritical Fluid Solvents

The use of reverse micelle supercritical fluid solvents has been qualitatively explored for extraction of polar compounds from aqueous solvents. For instance, at 100 °C and 250 bar a polar dye (Basic Red No. 5) can be extracted from an aqueous phase with a supercritical propane-reverse micelle solution (50 mM AOT). The extraction efficiency is strongly dependent on pressure and there is a threshold pressure (~250 bar) where the extraction efficiency increases abruptly. In addition to pressure, both pH and ionic strength affect the partitioning of a polar solute between the two phases. From our preliminary studies it also appears that increasing the overall volume fraction of the aqueous phase decreases the extraction efficiency.

By exploiting the pressure-dependent partitioning of polar species between aqueous and supercritical fluid-reverse micelle phases, extraction and solute recovery processes may be simplified. More extensive studies are currently in progress to better define the properties and applications, of these systems for extractions from aqueous phases.

CONCLUSIONS

Initial results with reverse micelle supercritical fluid separations have been encouraging and indicate that continued study of their application is warranted. For chromatographic applications results have shown that retention times of polar solutes are substantially reduced using a micellar mobile phase, allowing more polar solutes to be separated with SFC. The higher efficiencies obtained using a reverse micelle supercritical fluid mobile phase are more representative of pure fluid systems than of liquid reverse micelle phases. The effect of pressure on retention remains to be more fully examined for reverse micelle SFC applications. Reverse micelle supercritical fluid solvents also offer similar potential advantages in a variety of extraction and separation processes. It is anticipated that selectivity may be adjusted using pH, ionic strength, or supercritical fluid pressure to control solute-micelle partitioning, similar in manner to that used in controlling selectivity in extraction processes for separating amino acids and proteins in liquid systems (3,4,6).

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