Investigation of Cosolvent Effects on the Solvation of AOT Reverse Micelles in Supercritical Ethane

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We present spectroscopic evidence of the preferential solvation and penetration of the cosolvents benzene and methylene chloride into the surfactant tail regions of AOT reverse micelles in supercritical ethane. The micropolarities on both sides of the AOT surfactant interface were investigated using the UV−vis absorption probes phenol blue and methyl orange. Phenol blue was identified to reside in the surfactant tail region of the AOT reverse micelles, and its wavelength of maximum absorption remained sensitive to property changes in the ethane continuous phase. Furthermore, the preferential penetration of cosolvents benzene and methylene chloride was observed as evidenced by a synergistic effect (enhanced red shift) on the phenol blue absorption spectra over the experimental pressure range. Studies with the probe methyl orange, which resides in the reverse micelle core, further showed that, while the composition of benzene is enhanced in the surfactant tail region, benzene did not penetrate the reverse micelle core.

Introduction

Supercritical fluids (SCFs) have received much attention in the past two decades as solvents for separations,[1−3] as reaction media,[4] as a means of fine particle formation,[5,6] and in many other applications. This attention stems primarily from the ability to dramatically change such bulk physical properties as density, solute capacity, diffusivity, and viscosity with small variations in temperature and pressure. Unfortunately, many SCF applications that involve low critical temperature fluids are limited by low solubilities of ionic, highly polar, or high molecular weight molecules. An alternative of contemporary interest to increase these solubilities involves the formation of so-called water-in-oil microemulsions or reverse micelles by adding nonionic or ionic surfactants,[7] such as the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (known as AOT). Previous studies of reverse micelle systems in SCFs have shown the ability to solubilize hydrophilic substances including biomolecules[8−12] and dyes,[7,13−16] opening the door to many new applications.[17]

Figure 1 shows the structure of the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate, or AOT, which readily forms reverse micelles and microemulsions of water in alkane solvents. In addition, AOT also readily forms small reverse micelles in the absence of water in a variety of hydrocarbon solvents with aggregation numbers between 20 and 30[18,19] with a spherical to slightly ellipsoidal shape.[19,20] These will be referred to herein as "dry" reverse micelles.

AOT reverse micelles are thermodynamically stable aggregates of the amphiphilic surfactants, resulting in a hydrophilic headgroup region with hydrophobic tails that extend into a nonpolar continuous phase. A schematic diagram of a fully developed AOT reverse micelle in a supercritical fluid is shown in Figure 2. This reverse micelle is characterized as having a polar core (or "water pool") which is stabilized by a curved monolayer of the surfactant with its hydrophobic tails extending into the nonpolar continuous phase. The "water pool" is separated from the AOT headgroups by what has been referred to as the "palisade region" which contains most of the positively charged counterions.[21] This arrangement permits partitioning of ionic and polar molecules between the micelle core and a low-polarity medium. The micelle core is characterized by the ratio of water-to-surfactant molecules in the solution, W_o ($W_o = [H_2O]/[\text{surfactant}]$). In the present paper we report on "dry" reverse micelle systems, meaning that no additional water is added to the surfactant−solvent system.

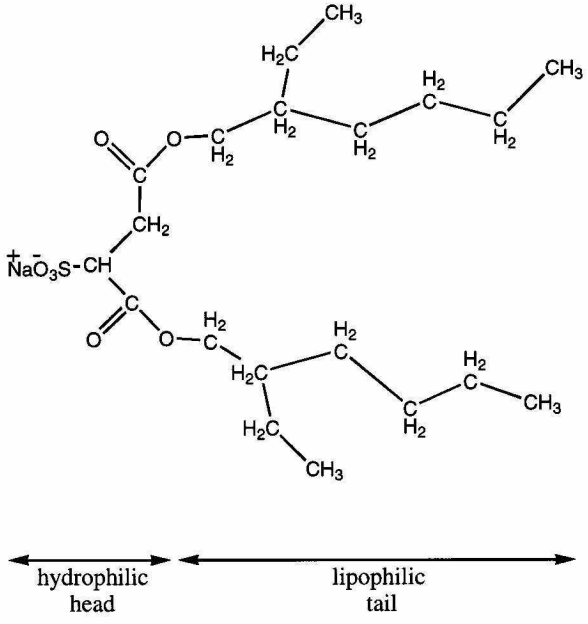

Figure 1. Structure of AOT (sodium bis(2-ethylhexyl) sulfosuccinate) surfactant.

While there has been a tremendous number of studies on reverse micelles and microemulsions in liquid solvent systems, studies of AOT microemulsions in SCFs have only appeared in the literature[7−13,16,22−32] since their discovery by Gale et al. in 1987.[7] The ability to adjust physical properties of SCFs over

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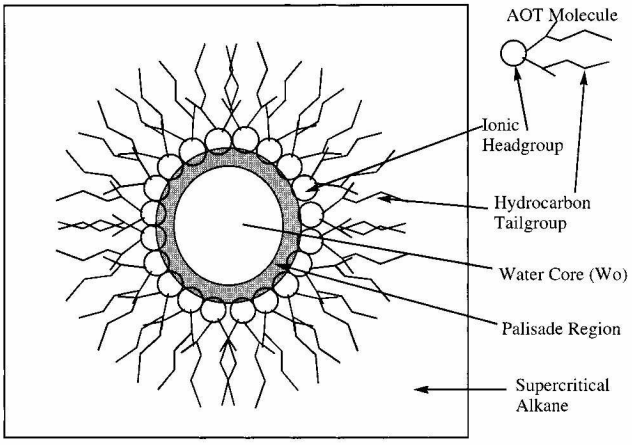

Figure 2. Schematic diagram of the structure of an AOT reverse micelle in a supercritical alkane solvent at an arbitrary water content, W_o = [water]/[AOT].

a continuum has permitted more detailed investigations into the general nature of reverse micelles and microemulsions.

Gale et al.[7] in 1987 reported the first observations of reverse micelles and microemulsions in SCFs using as their primary experimental method the visual observation of the solubility of polar, colored dyes in SCF−AOT−water systems. This initial study suggested the ability to create a broad range of organized molecular assemblies in dense gas and SCF solvents where the readily variable properties of the fluids could be exploited. There has been continuous progress toward improving our comprehension of these AOT reverse micelle systems in SCFs since this first report by employing an assortment of techniques including dynamic light scattering, small-angle neutron scattering, FT-IR, UV−vis, fluorescence, and time-resolved fluorescence spectroscopy.[7−13,16,21−32] In general, these works have shown the ability to produce thermodynamically stable reverse micelles for which there is essentially no change in the size and interior polarity of AOT reverse micelles with changes in pressure in a single-phase system, but that attractive interactions (micelle−micelle) may become enhanced at low pressures.

Solvatochromic Absorption Probes. The size, shape, and interior polarity of reverse micelles can be measured with a variety of spectroscopic probes, including solvatochromic UV−vis absorption probes and dyes. Solvatochromic absorption probes are extremely sensitive to their local environment and can be used to characterize the various microdomains within a microemulsion. These probes report this sensitivity through changes in the wavelength of maximum absorption, λ_{max}, of their absorption band. Due to their ability to report on the micropolarities within the aggregate, probes incorporated within reverse micelles can be used to deduce meaningful information about the distribution of the probe, water, and solvent molecules within the aggregate. The present work employs two different solvatochromic absorption probes located in different regions of dry AOT reverse micelles in SCF ethane.

For examples, Schelly and co-workers[33−35] used methyl orange [$(CH_3)_2NC_6H_4N{=}NC_6H_4SO_3Na$] and QB [1-methyl-8-oxyquinolinium betaine) to probe aggregation and solvent penetration into aggregates of the nonionic surfactant TX-100 in cyclohexane, benzene, and n-hexane. These hydrophilic probes were found to reside in the interior or core of the reverse micelles. El-Seoud and co-workers[36,37] have used a variety of UV−vis indicators, such as thymol blue and malachite green, in an attempt to assign pH to reverse micelle water pools. In addition to using probes to characterize the core region of reverse micelles, certain probes can also be used to deduce information about the micelle interface. Reichardt's ET(30) probe has been used to study interactions at the surfactant interface of reverse micelles[38,39] while Fernandez and Fromherz[40] have also studied coumarin dyes at the interface of micelle systems.

Absorption probes have also been used to gain information about reverse micelle systems in supercritical fluid solvents. For example, using the absorption probe pyridine N-oxide coupled with the fluorescence probe 8-anilino-1-naphthalenesulfonic acid (ANS), Yazdi et al.[16] explored the possibility of pressure tuning of the polarity in AOT reverse micelle systems in SCF ethane and liquid propane in both one- and two-phase regions. Furthermore, the hydrophilic probe methyl orange has also been used to investigate the microenvironment in pentaethylene glycol n-octyl ether reverse micelles in SCF CO_2,[21] large (25 nm) poly(fluoroacrylate)-g-poly(ethylene oxide) reverse micelles in CO_2,[41] and PFPE water-in-CO_2 microemulsions.[17] There are many applications (e.g., emulsion polymerization) that may be more ideally conducted if possibly done in the nonflamable, inexpensive, and relatively nontoxic SCF CO_2. However, Consani and Smith[42] showed that most conventional alkyl-functional ionic surfactants (such as AOT) exhibit poor solubility in CO_2. Recently, investigators have designed, synthesized, and studied model surfactants specifically designed for use in CO_2[17,41,43−45] as well as the addition of cosurfactants to increase water uptake in reverse micelles in CO_2.[14] McFann et al.[14] used the solvatochromic probes methyl orange and 1-methyl-8-oxyquinolinium betaine to investigate the effect of pressure on aggregation number and the effect of surfactant concentration on aggregation mechanism in SCF CO_2. Ionic dyes were also used to study the pressure effect on size and structure near the phase boundary. With these developments in reverse micelle formation and surfactant solubility in SCFs, many unique applications are on the horizon.[17]

Cosolvents and Cosurfactants. The addition of small amounts of cosolvent with a volatility intermediate to that of the solute and SCF can increase the solubility of the solute while maintaining the favorable properties of the fluid.[2,46] The cosolvent addition furnishes the ability to tune solvent properties for specific applications.[2,46] Cosolvents and cosurfactants have also been used in reverse micelle systems to promote aggregation, increase surfactant solubilities, and increase water uptake in the cores. For instance, medium chain length alcohols, often referred to as cosurfactants, have been added to liquid[47] and SCF[14] reverse micelle solutions. Although there is much debate in the literature as to the exact reason for the alcohol effect, most studies suggest that the alcohol inserts itself between surfactant tails, reducing tail−tail and micelle−micelle interactions. Some very hydrophilic alcohols such as ethanol can partition into the water core of liquid reverse micelles.[48] The effects of added cosolvents and cosurfactants have also been exploited in SCF systems. In SC ethane/AOT systems, low concentrations of the cosurfactant octanol have resulted in dramatic increases in W_o^{sat} at reduced pressures[11] while other cosolvents such as octane have also been used to achieve pressure reductions in SCF systems.[21]

In some work very pertinent to this paper, Zhu and Shelly[33] reported a study of the microenvironment and water distribution in reverse micelles of the nonionic surfactant Triton X-100 in mixed liquid solutions of 30% (v/v) benzene and 70% (v/v) n-hexane using the absorption probes methyl orange (MO) and 1-methyl-oxyquinolinium (QB). The results suggested the preferential penetration of benzene into the dry Triton X-100

reverse micelle cores, leaving the bulk benzene/n-hexane solvent depleted of benzene.

In this study, we focus on the effects that added cosolvents, such as benzene and methylene chloride, have on the solvation of "dry" AOT reverse micelles and, in particular, the tail regions of these reverse micelles in SCF ethane. Since the AOT surfactant system has received the most attention in SCFs to date, we have chosen it for our investigations concerning the effects of added cosolvents on reverse micelle tail solvation. By using UV−vis absorption probes that reside in different areas of the micelle structure (core, palisade, tails, etc.), we can report on the preferential solvation effects on the micelle tails by the cosolvents and on the integrity of the micelles under these conditions. The present study was designed, in part, to explore short-range interactions between solvent and the surfactant tails and cosolvent and surfactant tails and to explore the possibility of penetration of the cosolvents into the micelle core. Specifically, the probe phenol blue was used to explore the solvation of the micelle tail region and the effects of preferential penetration of the tails by cosolvents such as benzene and methylene chloride. The probe methyl orange was also used to explore the micelle core region and to examine micelle integrity and degree of cosolvent penetration.

Experimental Section

Materials. The anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was purchased from Fluka (Purum grade, >98%) and used as received. The surfactant retains a small amount of residual water, and this "as-received" condition for the AOT is designated as $W_o = 1$. Care was taken to ensure that the AOT received from the supplier absorbed no additional water and was verified using baseline spectra of the absorption probes described within. Benzene and methylene chloride were obtained from Aldrich and used as received. CP grade ethane ($T_c = 32.2$ °C, $P_c = 48.8$ bar) was purchased from BOC Gases. The probes phenol blue (N,N-dimethylindoaniline) and methyl orange were obtained from Eastman and Aldrich, respectively, and used without further purification.

Spectroscopic Investigations. The UV−vis spectroscopic studies were conducted in a custom 128 mL constant volume optical cell with a fixed path length of 7 cm mounted on an adjustable stage to provide precise alignment and reproducible spectra. The stainless steel cell (measuring 2 in. i.d. by 4.5 in. deep and $2^7/_8$ in. o.d. by 5.5 in. high) was fitted with 0.75 in. diameter by 0.3 in. thick UV grade windows. The large path length resulted in a measurable absorbance with only a minimal amount of probe in the cell ($<1 \times 10^{-6}$ M), thus perturbing the micelle system as little as possible. Reverse micelle solutions of known concentration were prepared by loading AOT and the appropriate solvatochromic probe directly to the cell. The cell was then sealed and pressurized with a 266 mL Isco 260D syringe pump. For experiments with ethane−cosolvent mixtures, a desired amount of ethane was first condensed into the Isco syringe pump. An Eldex model B-100-S metering pump was then used to charge a known quantity of cosolvent. The mixture was allowed to equilibrate for at least 16 h and then charged to the optical cell. Spectroscopic experiments were always performed in the order of increasing pressure such that the molar concentration of the AOT remained constant. Pressure was measured to ±0.2 bar with a digital Heise pressure gauge. A heating tape, platinum RTD, and an Omega temperature controller were used to maintain the cell temperature to within ±0.1 °C. The solution was agitated directly in the sample compartment of the UV with a 0.5 in. long magnetic stir bar and a micro-electromagnetic stirrer.

TABLE 1: Wavelength of Absorption Maximum (λ_m) of Phenol Blue in Various Systems

solvent	λ_m
cyclohexane	550
benzene	575
methanol	608

Absorption spectra were measured with a Varian Cary 3E UV−vis spectrophotometer. Absorption spectra were obtained by averaging a minimum of 10 scans and by subtracting an average baseline spectrum collected at the same conditions in the absence of the probe. The wavelength of maximum absorption, λ_{max}, was determined by fitting the spectra with a polynomial. Typical uncertainty in λ_{max} was ±0.2 nm. For experiments in which a SCF phase was in equilibrium with a surfactant-rich phase, the beam of the spectrophotometer passed through the fluid phase alone and did not contact the surfactant-rich phase on the bottom of the cell.

Results and Discussion

A solvatochromic probe, when incorporated within a reverse micelle, can yield structural information about the micelle and its environment. These probes can be extremely sensitive to their immediate environment, and it is necessary to obtain specific information about a probe in order to properly interpret data from these solvatochromic probes. It is important to verify that the probe does not perturb the system being studied, to determine the location of the probe within the reverse micelle aggregate, and to determine the specific features of its surroundings the probe is sensitive to.[21]

Determination of the actual location of the probe within the surfactant aggregate is often very difficult. In the context of our simplified model of an AOT reverse micelle given in Figure 2, a probe can be located in the water pool, in the palisade region, or among the surfactant tails. Many probes contain both polar and nonpolar moieties and are, therefore, attracted to some degree to the surfactant interface.

Phenol blue proved to be a suitable solvatochromic dye to study solvent−tail and cosolvent−tail interactions because the probe resides in the surfactant tail regions of fully developed AOT reverse micelles, as illustrated below. Similar behavior was observed for the $E_T(30)$ probe in liquid reverse micelle solutions.[38,39] Phenol blue has a single intense absorption band at ≈550 nm in cyclohexane, corresponding to a $\pi \rightarrow \pi^*$ transition. The red shift of the absorption maximum (seen for several example solvents in Table 1) exceeds 55 nm in going from a nonpolar to a polar protic solvent, illustrating its sensitivity.

Figure 3 illustrates the change in λ_{max} for phenol blue in pure ethane and in a 0.01 M AOT−ethane mixture at various pressures at 37 °C. From 61 to 100 bar, λ_{max} in the 0.01 M AOT−ethane mixture (upper curve) is shifted relatively little compared to its values in pure ethane seen as the lower curve. This suggests that the fluid phase contains premicellar aggregates such as are seen at low surfactant levels in liquid solvents. Above 100 bar, phenol blue senses an environment of increasing polarity in the 0.01 M AOT−ethane mixture, and λ_{max} increases more dramatically above the pure ethane baseline until, at 148 bar, all of the loaded AOT is solubilized and the system becomes one phase. In this region the concentration of AOT is sufficient for reverse micelles to form, and solubilization increases rapidly. This transition at 148 bar correlates well with visual observations of AOT cloud points performed in our laboratory.[49] Notice that

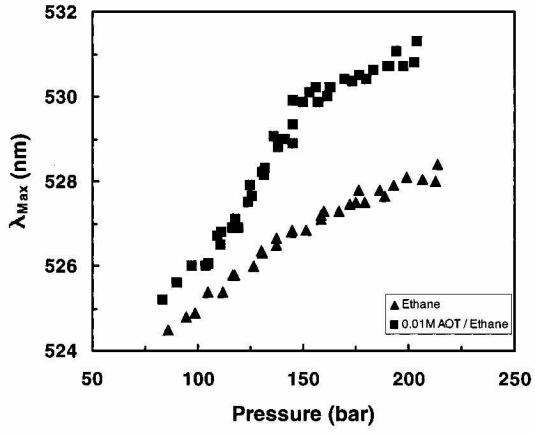

Figure 3. Wavelength of maximum absorption, λ_{max}, of phenol blue probe in pure ethane (▲) and in a 0.01 M AOT−ethane mixture (■) as a function of pressure. T = 37 °C.

above 148 bar, although phenol blue senses an environment of increased polarity in the system with reverse micelles (upper curve), it remains sensitive to the solvent strength of the continuous phase. In this region, the λ_{max} curve for phenol blue in the 0.01 M AOT−ethane mixture follows the same general trend as that of phenol blue in pure ethane, with an increase in λ_{max} with an increase in pressure. Previous studies with solvatochromic probes have described the polarity of the interior of dry reverse micelles as methanol-like.[15] Phenol blue has an absorption maximum of 608 nm in methanol whereas its maximum absorption in this 0.01 M AOT reverse micelle system is slightly greater than 530 nm. This suggests that the phenol blue resides in a more hydrocarbon-like environment. For this reason and the fact that λ_{max} remains sensitive to the bulk solvent strength, it is very unlikely that phenol blue is localized in the reverse micelle interior. Probes that are localized in the micelle interior, such as pyridine N-oxide,[16] are virtually insensitive to changes in bulk environment once the AOT reverse micelles are formed. A more probable explanation of the phenol blue experimental data in Figure 3 would be localization of the probe in the surfactant tail region. This model explains both the increased polarity "felt" by the probe as it interacts with the reverse micelle aggregate compared to the pure solvent, as well as its continuing sensitivity to the changing solvent strength of the continuous phase as pressure is increased.

Having identified a solvatochromic probe localized on the solvent side of the micelle interface, this probe can be used to directly investigate the effect of added cosolvents on micellar phenomena in supercritical fluids. Benzene was chosen as one of the cosolvents in this study for a number of reasons. Previous work indicated that, for at least several surfactant systems, benzene would interact with the AOT surfactant headgroup region. Using laser photolysis, Atik and Thomas[50] studied reverse micelle systems of AOT and showed that various additives affect the rate of ion transport that occurs when reverse micelles collide. Benzene was found to decrease the effectiveness of solute penetration, suggesting that it interacts in the surfactant headgroup region, producing a more compact structure with a more rigid interface. A more recent study by Zhu and Schelly[33] described the preferential penetration of benzene into the cores of reverse micelles of the nonionic surfactant TX-100, leaving the bulk benzene/n-hexane solvent depleted of benzene. Based on these previous studies and given the enhanced local environment that can occur in supercritical fluid solutions,[51] a cosolvent effect by adding benzene to the AOT−ethane systems could be anticipated.

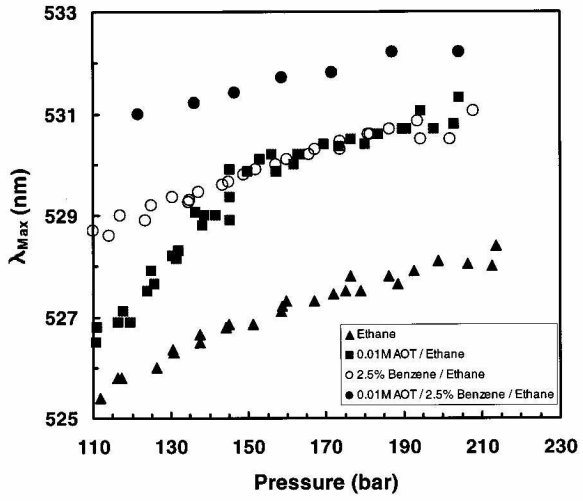

Figure 4. Wavelength of maximum absorption, λ_{max}, of phenol blue probe in pure ethane (▲) and in a 0.01 M AOT−ethane mixture (■), in 2.5 mol % benzene−ethane mixture (○), and in 0.01 M AOT−2.5 mol % benzene−ethane mixture (●). T = 37 °C.

The dramatic effects of adding 2.5 mol % benzene to a 0.01 M AOT−ethane system on the λ_{max} of phenol blue are seen in Figure 4. As discussed earlier, cosolvents can be used to achieve pressure reductions in SCF systems. The addition of 2.5 mol % benzene to the 0.01 M AOT−ethane system lowers the cloud point to 120 bar, such that only the one phase is shown in Figure 4 for pressures between 120 and 230 bar. The upper trace does indeed show the same general shape as that of the 0.01 M AOT in pure ethane curve with the cloud point shifted to 120 bar. As in Figure 3, the lowest curve in Figure 4 depicts the behavior of λ_{max} of phenol blue in pure ethane. As pressure is increased, the solvent strength of the ethane increases and is reflected by an increase in the λ_{max} for phenol blue. Addition of 2.5 mol % benzene to the ethane solvent further enhances the solvent strength of the medium and essentially shifts the λ_{max} of phenol blue in pure ethane to higher wavelengths of maximum absorbance. Interestingly, the environment sensed by phenol blue in the surfactant tail groups of a 0.01 M AOT system in ethane roughly corresponds to that of a 2.5 mol % benzene−ethane mixture, giving some indication of the solvent strength "felt" by the probe in the AOT reverse micelles. Addition of 2.5 mol % benzene to a 0.01 M AOT−ethane system results in λ_{max} values of phenol blue that are yet higher than those in either the 0.01 M AOT−ethane system (when the probe is in the reverse micelle tails) or the 2.5 mol % benzene−ethane system. This is interesting in that solvent strength, or micropolarity, is not additive. As an example, one would not expect the probe to report a higher λ_{max} in a mixture of a polar and a nonpolar solvent than in either of the pure solvents. The synergistic effect obtained by adding benzene to the fully developed micelles in the AOT−ethane system can be explained by preferential penetration of benzene into the surfactant tail groups, thus resulting in an increased micropolarity.[33] Similar behavior was observed for other benzene compositions, although the effect is not as dramatic. These results might suggest an optimal range in benzene composition for this preferential solvation effect.

This synergistic effect is also observed at other benzene cosolvent concentrations. Figure 5 shows the effect of the addition of 1.5 mol % benzene to the 0.01 M AOT−ethane system. Again, an enhanced λ_{max} for phenol blue is observed when 1.5 mol % benzene is added to the 0.01 M AOT−ethane system compared to the 0.01 M AOT−ethane system and to

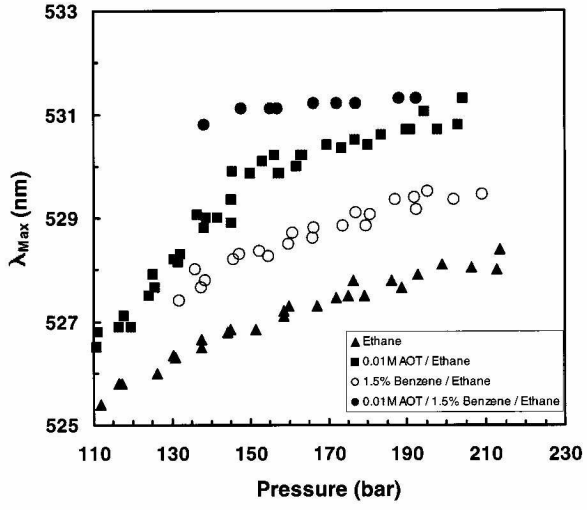

Figure 5. Wavelength of maximum absorption, λ_{max}, of phenol blue probe in pure ethane (▲) and in a 0.01 M AOT−ethane mixture (■), in 1.5 mol % benzene−ethane mixture (○), and in 0.01 M AOT−1.5 mol % benzene−ethane mixture (●). T = 37 °C.

the 1.5 mol % benzene−ethane system. This again suggests the preferential solvation of the reverse micelle tails by benzene cosolvent.

To examine the degree of this effect, a plot of λ_{max} of phenol blue as a function of benzene composition in ethane−benzene mixtures with and without the addition of 0.01 M AOT is shown in Figure 6. The measurements shown in Figure 6 were performed at 37 °C and 159 bar. At this temperature and pressure, the λ_{max} of phenol blue in pure ethane is 527.2 nm while λ_{max} in the 0.01 M AOT−pure ethane system is 529.8 nm. This corresponds to a 2.6 nm red shift of phenol blue's λ_{max} upon the formation of the AOT reverse micelles with the probe located in the micelle tail region. The corresponding red shift in λ_{max} upon the formation of AOT reverse micelles in pure benzene is 1.2 nm. Interestingly, in a 2.5 mol % benzene−ethane mixture, there is only a 1.4 nm red shift of λ_{max} with the addition of 0.01 M AOT to the mixed solvent. This is rapidly approaching the pure benzene limit of a 1.2 nm shift with as little as 2.5 mol % benzene addition. This suggests that even with this small loading of benzene to the 0.01 M AOT−ethane system, the probe senses an enhanced benzene environment, potentially approaching near saturation in the tail region with benzene cosolvent. If the ethane−benzene mixtures were to behave ideally, meaning no preferential solvation effects occurred, one would expect the λ_{max} of phenol blue to increase in the 0.01 M AOT−ethane−benzene mixtures with the same slope as the ethane−benzene curve in Figure 6. However, the increase of λ_{max} with added benzene in the reverse micelle system (upper curve) is less steep than simply in the mixed solvent system (lower curve), and the separation of the two curves rapidly approaches the 1.2 nm limit at low (<4 mol %) benzene compositions.

The cosolvent methylene chloride was also explored in order to examine the generality of the benzene cosolvent experiments. Figure 7 shows the effect on λ_{max} of the addition of 1.6 mol % methylene chloride to pure ethane and to the 0.01 M AOT−ethane system. Methylene chloride was chosen as a cosolvent as it is a relatively small, polar molecule for which an enhanced penetration into the AOT reverse micelle tails might be anticipated. Once again, Figure 7 plots λ_{max} of phenol blue as a function of pressure in pure ethane and in the 0.01 M AOT−ethane system. The addition of 1.6 mol % methylene chloride to the ethane solvent again further enhances the solvent strength of the medium and shifts the λ_{max} of phenol blue to higher wavelengths. In this case, the environment sensed by phenol blue in the surfactant tail groups of a 0.01 M AOT reverse micelles in pure ethane system roughly corresponds to that in a 1.6 mol % methylene chloride−ethane solvent mixture. Furthermore, the addition of 1.6 mol % methylene chloride to the 0.01 M AOT−ethane system again results in λ_{max} values that are further red-shifted than in either the 0.01 M AOT−ethane system or the 1.6 mol % methylene chloride−ethane solvent mixture. This can be explained by the preferential solvation and penetration of the polar cosolvent into the tail groups of the fully developed AOT reverse micelles, resulting in an increased micropolarity due to the locally increased composition of the cosolvent. By comparison, similar synergistic shifts are observed with the addition of 1.6 mol % methylene chloride and with the addition of 2.5 mol % benzene (Figures 4 and 7). This more dramatic effect with the methylene chloride

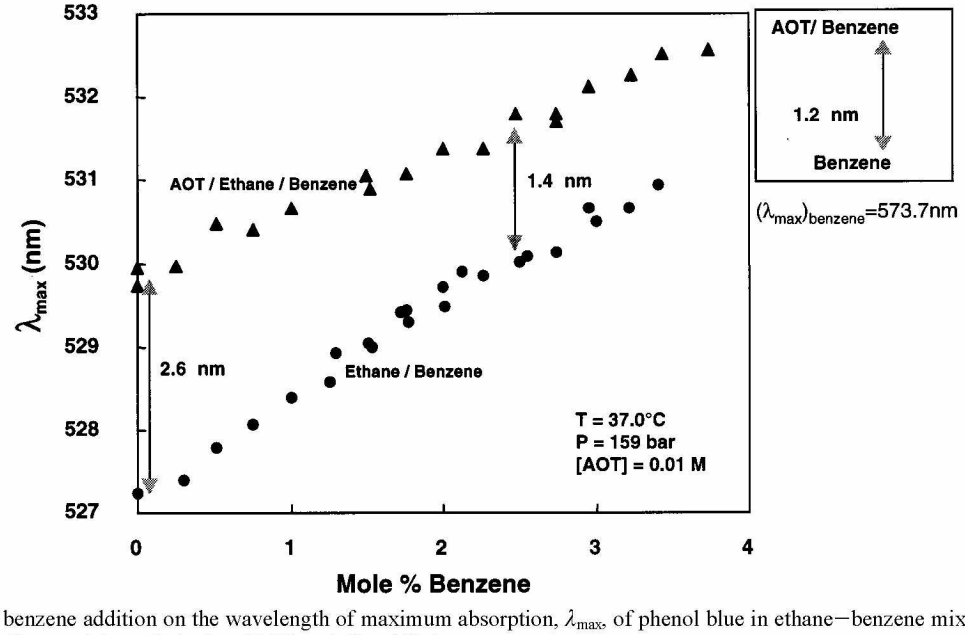

Figure 6. Effect of benzene addition on the wavelength of maximum absorption, λ_{max}, of phenol blue in ethane−benzene mixtures (●) and in 0.01 M AOT−benzene−ethane mixtures (▲). T = 37 °C and P = 159 bar.

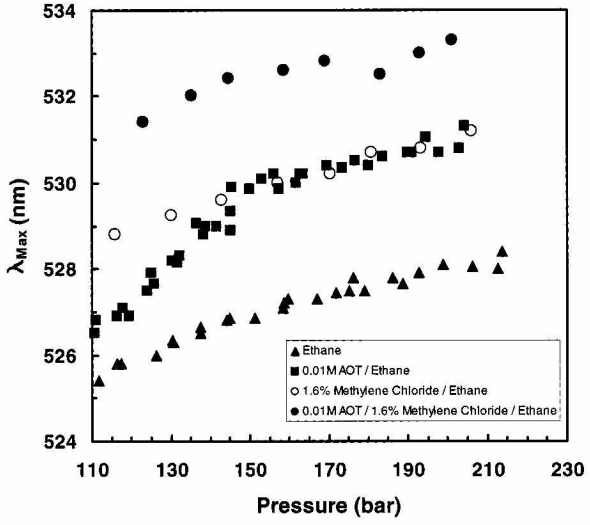

Figure 7. Wavelength of maximum absorption, λ_{max}, of phenol blue probe in pure ethane (▲) and in a 0.01 M AOT−ethane mixture (■), in 1.6 mol % methylene chloride−ethane mixture (○), and in 0.01 M AOT−1.6 mol % methylene chloride−ethane mixture (●). T = 37 °C.

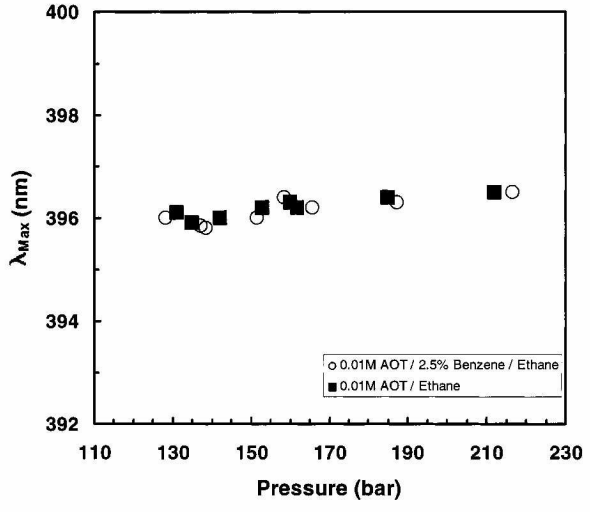

Figure 8. Wavelength of maximum absorption, λ_{max}, of methyl orange probe as a function of pressure in reverse micelles of a 0.01 M AOT−ethane mixture (■) and in a 0.01 M AOT−2.5 mol % benzene−ethane mixture (○). T = 37 °C.

cosolvent could be attributed to the fact that the small, polar methylene chloride molecule may be more attracted to the surfactant interface.

Using a second solvatochromic probe (methyl orange) known to partition into the interior of AOT reverse micelles, the extent of the benzene penetration was explored. In this case, the probe in harbored in the core and is essentially protected from changes in the continuous phase. As can be seen in Figure 8, the addition of 2.5 mol % benzene to a 0.01 M AOT system has no effect on the λ_{max} values reported by methyl orange, suggesting that benzene only clusters around the reverse micelle but does not actually penetrate the reverse micelle core. Using the same probe, Zhu and Schelly[33] found that, for the nonionic surfactant TX-100, benzene actually penetrates the micelle core. This difference can be attributed to the structure of these two different surfactants. AOT has an ionic headgroup that is essentially a point charge, whereas the headgroup for TX-100 is a nonionic polyoxyethylene chain. The interaction between the highly polarizable benzene and the polyoxyethylene chain is very strong, resulting in penetration of the reverse micelle core. In the case of the AOT, while attracted to the micelle tail region and potentially to the interface to some degree, the benzene does not penetrate the barrier provided by the more rigid headgroup structure of the AOT reverse micelles in SCF ethane.

Conclusions

An appropriate solvatochromic probe has been identified that resides in AOT reverse micelle tails in SCF ethane. The preferential penetration of the cosolvents benzene and methylene chloride into the AOT reverse micelle tails as evidenced by a synergistic effect on phenol blue absorption spectra was observed. Furthermore, investigations with the probe methyl orange, which resides in the core of the reverse micelle, have shown that while the benzene clusters around the reverse micelle and preferentially penetrates the tails, it does not penetrate into the reverse micelle core. These results illustrate the ability to use cosolvents to preferentially solvate reverse micelles in SCF/cosolvent systems.

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