Solubilization in Nonionic Reverse Micelles in Carbon Dioxide

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Phase behavior data and FTIR spectra along with solubilities and solvatochromic shifts of ionic indicator dyes are reported for binary, ternary and quaternary systems composed of pentaethylene glycol n-octyl ether (C_8E_5), CO_2, water, and n-pentanol as a function of temperature, pressure and composition. With the addition of n-pentanol as a cosurfactant, the water to surfactant ratio, W_o, reaches values as high as 12. As water is added further, a surfactant-rich phase precipitates due to micelle-micelle interactions. Ionic dyes are soluble at levels of 0.03 mM, far in excess of the negligible solubility in pure CO_2.

Introduction

Carbon dioxide is an attractive alternative to certain organic solvents, since it is nontoxic, nonflammable, inexpensive, and relatively nonpolluting. Examples of interesting applications based on compressed and supercritical CO_2 include spray painting (Nielsen et al., 1990), polymerization (DeSimone et al., 1992), particle formation by rapid expansion from supercritical solution (Debenedetti, 1990), and precipitation with a compressed fluid antisolvent to form microparticles and fibers (Dixon et al., 1993; Dixon and Johnston, 1993). A limitation is that high molecular weight or hydrophilic molecules are often insoluble in supercritical CO_2. Hydrophilic substances, such as amino acids and proteins, may be solubilized in reverse micelles and microemulsions in supercritical alkanes (Fulton et al., 1989; Johnston et al., 1989b; Eastoe et al., 1990; Kaler et al., 1991; Lemert et al., 1990; McFann and Johnston, 1991). In these systems, hydrophilic solutes partition into the polar cores and interfacial regions of the reverse micelles and are shielded from the nonpolar solvent by the surfactant interface (Leodidis et al., 1991; Lemert et al., 1990). The size, shape and interior polarity of reverse micelles have been measured with a variety of UV-visible (Zhu and Schelly, 1992; Zhu et al., 1992; Ueda and Schelly, 1989; El Seoud et al., 1982; Schanze and Whitten, 1983) and fluorescence (Zana, 1987; Yazdi et al., 1990; Zhang and Bright, 1992; Kalyanasundaram, 1987) probes. Theoretical models agree with experimental data and have been used to explain the mechanism of pressure effects on the droplet size and phase behavior of microemulsions in compressed fluids (McFann and Johnston, 1991; Peck and Johnston, 1991, 1993; Peck et al., 1991; Kraus and Panagiotopoulos, 1992).

Initial studies indicate that the aggregation of surfactants to form reverse micelles in CO_2 is much more limited than in compressed alkanes such as ethane and propane (Oates, 1989; Iezzi et al., 1989; Ritter and Paulaitis, 1990; Consani and Smith, 1990). The same lack of solvent strength that prevents direct solubilization of hydrophiles also hinders the solubility of surfactants, particularly ionic ones. Consani and Smith (1990) tested the solubility of over 130 commercially available surfactants in supercritical CO_2 at 50°C and 100–500 bar. Practically all of them were insoluble or only slightly soluble, and they did not solubilize a significant amount of water. McFann (1993) found that certain surfactants solubilized excess water into CO_2 when cosurfactants are added. Nonionic surfactants are generally more soluble than ionics. The partitioning behavior of a variety of polyethylene glycols of varying molecular weights in a system also containing CO_2 has been measured and modeled theoretically (Daneshvar and Gulari, 1989). Eckert et al. (1992) have studied the fractionation of nonionic surfactants with supercritical fluids.

Yee et al. (1992) studied the aggregation of $C_{12}E_3$ and $C_{12}E_8$ in compressed solvents without added water using FTIR spectroscopy. They found the aggregation number of $C_{12}E_3$ to be

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approximately four in both CO_2 and ethane. Gupta and Johnston (1993) found with FTIR spectroscopy that an inert supercritical fluid, SF_6, influences hydrogen bonding between a donor and acceptor, and showed how this effect can be included in thermodynamic models. The free energy of hydrogen bonding is stabilized by a decrease in pressure, and the enthalpic interaction becomes stronger.

Hoefling et al. (1991) synthesized surfactant derivatives with fluorinated tails, which increased markedly their affinity for CO_2. A fluorinated sulfosuccinate was shown to dissolve in CO_2 above a bulk aqueous phase and to extract the interfacially active dye thymol blue. The amount of water in the CO_2 phase was unknown, since this dye dissolves in dry reverse micelles (Fulton et al., 1989). This breakthrough offers the possibility that water and even more hydrophilic substances can be solubilized in a CO_2-based solvent with the aid of a carefully chosen surfactant system.

The objective of this work was to solubilize water and hydrophilic ionic dyes in CO_2 by using a nonionic surfactant in supercritical CO_2. We chose to study the nonionic surfactant pentaethylene glycol *n*-octyl ether, C_8E_5, since it is highly soluble in CO_2 and capable of solubilizing significant amounts of water because of the five ethylene oxide groups. The cosurfactant, *n*-pentanol, has the potential to enhance the formation of micelles and the water solubilization, based on studies in ethane (Johnston et al., 1989a,b; McFann, 1993). The phase boundaries are reported as a function of surfactant concentration, cosurfactant concentration, temperature, pressure, and amount of added water. Solvatochromic probes are used to examine the polarity of microdomains in the aggregates. Solubilities of dyes are measured and compared with the phase behavior and solvatochromic probe data to evaluate the aggregation of the surfactant. To further aid the interpretation of the results, the same types of experiments were performed with nonionic surfactants in conventional liquid hydrocarbon solvents.

Properties of CO_2 and Their Influence on Reverse Micelle Formation

Aggregation is brought about by a balance between the lateral interactions among surfactant molecules at the surfactant interface and the interactions between the surfactant and the solvent (Bourrel and Schechter, 1988; Peck et al., 1991). If the interactions are unbalanced, then the surfactant will be either insoluble or dispersed in solution as monomer. In the case of CO_2, this balance of forces has proven exceedingly difficult to achieve, primarily because of the special properties of CO_2 as a solvent. In general, the driving force for forming reverse micelles are much weaker than for normal micelles (Bourrel and Schechter, 1988). Therefore, the term reverse micelle will be used in this article for aggregates with as little as about 10 surfactant molecules.

A variety of properties of CO_2 must be taken into account in designing surfactant systems. CO_2 has a low dielectric constant compared to alkane supercritical fluids and to liquid solvents like pentane (Yee et al., 1992). Consequently, ionic surfactants are rarely soluble in CO_2 (Consani and Smith, 1990; McFann, 1993). Thus, this study focuses on nonionic surfactants. Furthermore, its polarizability and polarizability/volume are less than those of ethane and propane, so the solvation of long hydrocarbon surfactant tails is hindered. To overcome this limitation, Hoefling et al. (1991) studied ionic surfactants with fluorinated tails which can be solubilized by CO_2. The solubility parameter is another well-known criterion of solvent strength. Interestingly, the solubility parameter of CO_2, as calculated from the thermodynamic data of Din (1962), is actually higher than those of propane and ethane at pressures greater than 300 bar, as shown in Figure 1. However, a substantial contribution to the CO_2 solubility parameter, possibly as much as 20% (Myers and Prausnitz, 1965), is due to the large quadrupole moment (Prausnitz et al., 1986; Murthy et al., 1981). Although this quadrupole moment influences the properties of pure CO_2, such as the relatively high critical pressure, it is relatively unimportant for the interaction between CO_2 and hydrocarbon tails. When the contribution from the quadrupole moment is removed, the solubility parameter of CO_2 would be about equivalent to that of ethane, which is consistent with solvatochromic probe data (Johnston et al., 1989a).

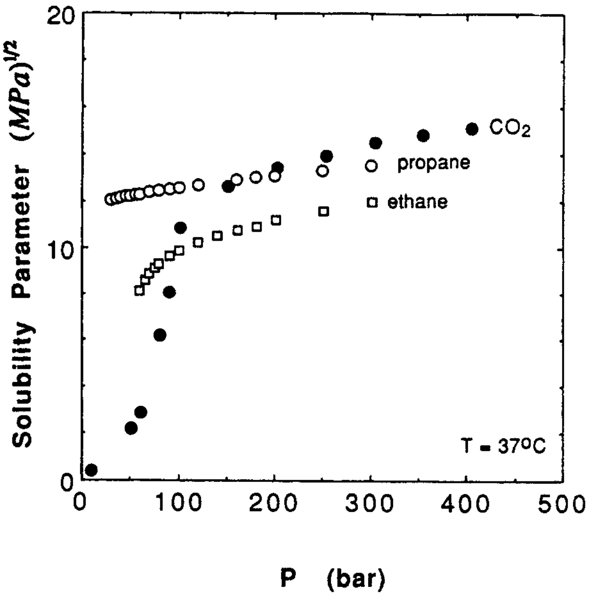

Figure 1. Solubility parameters of ethane, propane, and CO_2 at 37°C as a function of pressure.

Because of its quadrupole moment and Lewis acidity, CO_2 can take part in interactions that are not present in supercritical solvents such as ethane and propane. O'Shea et al. (1991) measured the tautomeric equilibrium of 4-(phenylazo)-1-naphthol in several supercritical fluids. They found a significant shift in favor of the more polar and basic hydrazone tautomer in CO_2 relative to ethylene and ethane, which may be attributed to polar forces and the Lewis acidity of CO_2. The interaction between CO_2 and basic hydroxyl groups has been studied with FTIR spectroscopy (Fulton et al., 1991). It is likely that these acid-base interactions may be important for ethoxylated nonionic surfactants in CO_2. If CO_2 displaces hydrogen bonds between surfactant head groups, which are a driving force for aggregation, it may inhibit surfactant aggregation, as has been observed for polar liquid solvents such as methanol and chloroform (Ravey et al., 1984).

Experimental Studies

Highly pure C_8E_5 (Sigma) and $C_{12}E_5$ (Nikko) were used without further purification. Brij 30, in which $C_{12}E_4$ is the major component, and Triton X-100, a poly(ethylene oxide) tetramethyl-butyl ether with an average of 9.5 ethylene oxide groups per molecule, are commercial products which were purchased from Aldrich. Carbon dioxide was Linde bone-dry grade. (99.8%). The solvatochromic indicator QB (1-methyl-8-oxyquinolinium betaine) was a generous gift from Professor Z. A. Schelly. The ionic dyes, methyl orange, methylene blue, and thymol blue, were obtained from Aldrich and used as received.

For spectroscopic experiments, surfactant solutions of known concentration were prepared in a 2-mL constant volume 6.35-cm-OD by 1.59-cm-ID stainless-steel cell fitted with two 2.54-cm-dia. × 0.95-cm-thick UV-grade sapphire windows. The path length was 1 cm. The cell was equipped with cartridge heaters and thermostated to ±0.1°C by a platinum resistance thermometer and an Omega temperature controller. Pressure was controlled to ±0.2 bar with a 60-mL syringe pump (High Pressure Equipment Co.). The surfactant and solvatochromic probe were introduced into the static cell as solutions in volatile solvents, so that final concentrations were known to be ±2%. The solvent was removed by evaporation, and water, if needed, was added with a 100-mL syringe after the cell had cooled down to its normal operating temperature. Experiments were always performed in the order of increasing pressure so that the overall molarities of surfactant, water and probe were constant.

FTIR spectra were collected at Nottingham using a Nicolet Instruments Model 730 Fourier transform interferometer (HgCdTe detector, 16k data points, nominal resolution 2 cm^{-1}). The high-pressure supercritical cell for infrared spectroscopy has been described earlier (Poliakoff et al., 1988; Howdle et al., 1990).

Variable volume view cells (28 mL) were used to determine the phase boundaries of C_8E_5 systems in CO_2 and to measure dye solubilization as a function of pressure (see Figure 2) as described previously (Lemert et al., 1990; McFann, 1993). By varying the volume of the surfactant solution with a piston, pressure and temperature may be varied independently while weight fractions remained constant. A recent refinement of the variable volume view cell apparatus was the addition of a motor-driven pump for injection of liquids through a sample loop of known volume in a six-port rotary valve (Valco). This speeds up the collection of experimental data considerably, as multiple concentrations can be evaluated without having to disassemble the view cell. The motor-driven injector contained a 1/8-in. (3.2-mm) plunger in a 1/4-in. (6.4-mm) cylinder. The seal was made with a 1/4-in. (6.4-mm) to 1/8-in. (3.2-mm) reducing union with teflon ferrules. The plunger cycled up and down between upper and lower limit switches. Injection techniques were used to measure the solubilization of water and the effect of cosurfactants on C_8E_5 aggregates in CO_2.

Results and Discussion

The emulsification efficiency of nonionic surfactants is related to the overall size of the surfactant molecule. The most effective surfactants have hydrocarbon tails with 12 carbons or more (Kahlweit et al., 1985, 1988, 1991). The C_{12} surfactants, however, are not very soluble in CO_2, because of its low polarizability/volume and dielectric constant (Consani and Smith, 1990; McFann, 1993). Thus, it was decided to use C_8E_5, which was found to be readily soluble. For the C_8E_5/octane/water system, the optimum temperature for complete water/oil emulsification is 62°C (Strey and Jonstromer, 1992), which means that the surfactant prefers water phases over oil phases at room temperature. However, it is just these kinds of surfactants that are most likely to form large aggregates in a nonpolar solvent (Ravey et al., 1984) because of the multiple hydrogen bonding sites on the poly(ethylene oxide) headgroups.

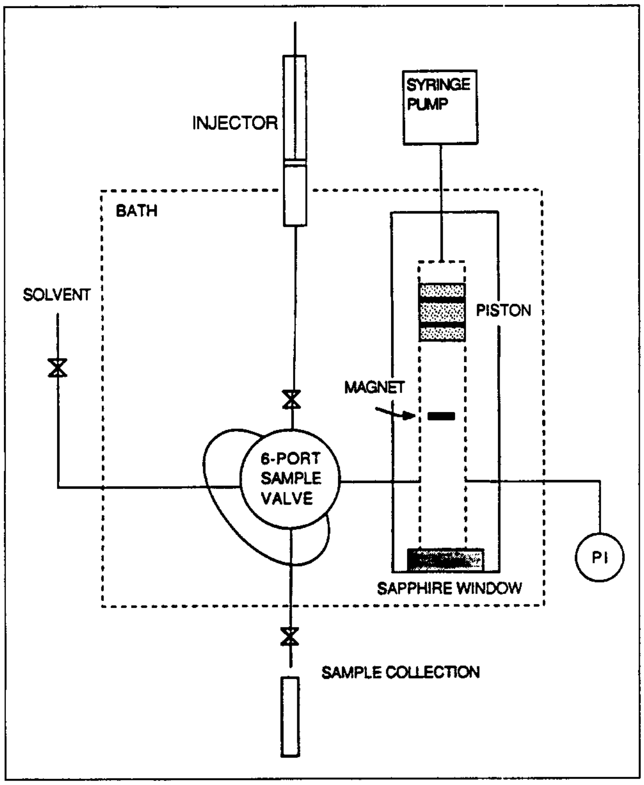

Figure 2. Variable volume view cell with external sampling loop and motor-driven injector.

Phase behavior in C_8E_5/water/CO_2 systems

The solubility of C_8E_5 in CO_2 is shown in Figure 3 as a function of CO_2 density. The systems are one phase for densities to the right of the lines and two phase to the left. As temperature increases from 20°C to 60°C, the density required to solubilize a given wt. % of surfactant decreases. This result is consistent with the well-known tendency of nonionic surfactants to become more oil-soluble as temperature increases, due in part to the breaking of hydrogen bonds between surfactant head groups (Shinoda and Friberg, 1986; Lindman and Wennerstran, 1991; Jonstromer et al., 1991). The solubility increases exponentially with density, a result seen for many types of molecules whether amphiphilic or not. The slopes of the curves suggest that C_8E_5 solubilities as high as 25 wt. % should be possible at experimentally accessible pressures (below 400 bar).

The difficulties in finding surfactants that will solubilize water in CO_2 are significantly greater than the problem of surfactant solubility itself. Consani and Smith (1990) discovered that even for those few surfactants that are appreciably soluble in CO_2, the addition of small amounts of water causes

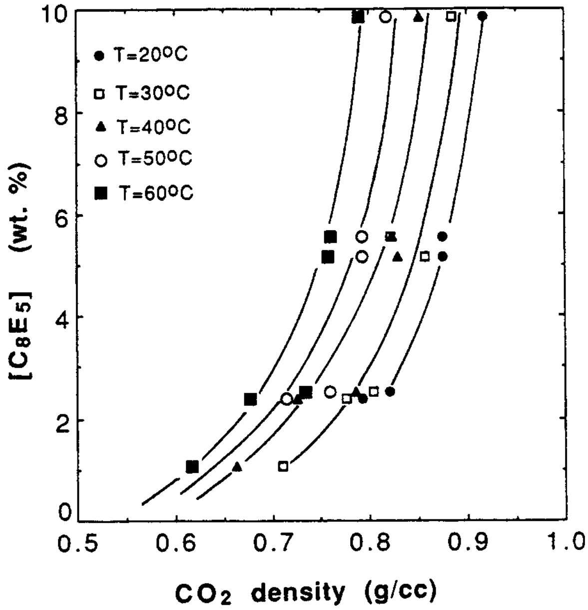

Figure 3. Solubility of C_8E_5 in CO_2 as a function of CO_2 density.

precipitation. This result is quite different from the behavior of nonionic surfactants in nonpolar liquids, where the addition of water normally facilitates surfactant solubility and aggregation (Ravey et al., 1984). The problem of water solubilization in surfactant/CO_2 systems is compounded by the fact that CO_2 itself has a significant affinity for water, far more than that of hexane or a compressed alkane like propane (Kobayashi and Katz, 1953; Wiebe, 1941). The water is distributed between surfactant and CO_2 in such a way as to minimize the overall free energy of the system. Eventually, as more water is added, a second phase forms. The phase separation is governed by the surfactant and solvent structures and by temperature (Hou and Shah, 1987; Averyard et al., 1989).

Figure 4 shows the phase boundaries for a 2.3 wt. % C_8E_5 system for various temperatures. The phase boundaries were determined for successive water injections into a fixed amount of C_8E_5 and CO_2. For comparison, the solubility of water in pure CO_2, indicated by horizontal lines for the same four temperatures, is relatively invariant with density over this range. At higher temperatures, lower densities are required to attain a one-phase system, just as in the water-free systems of Figure 3. At high CO_2 densities, the overall amount of water is significantly higher than the solubility of water in pure CO_2. Here, the slopes of the isotherms decrease markedly and a plateau is observed, suggesting that the aggregates are saturated with water.

The effect of temperature on the same system is shown in Figure 5 for a constant density of 0.85 g/cm^3. Here the water content is expressed in W_o, the molar water to surfactant ratio, based on the total water added. Some of the water is in bulk CO_2 and another part is associated with surfactant. As temperature increases, the amount of water associated with the surfactant increases much faster than that merely in bulk CO_2. A likely explanation for this increase in interactions between surfactant and water is that the aggregation number of surfactant increases, which is consistent with previous results for this surfactant with hydrocarbon solvents (Stey and Jonstromer, 1990).

Influence of a cosurfactant on phase behavior

Medium-chain-length alcohols have been used often to increase the size and solubilization capacity of reverse micelles and water-in-oil microemulsions. There has been debate in the literature as to the exact reason for the alcohol effect. Most

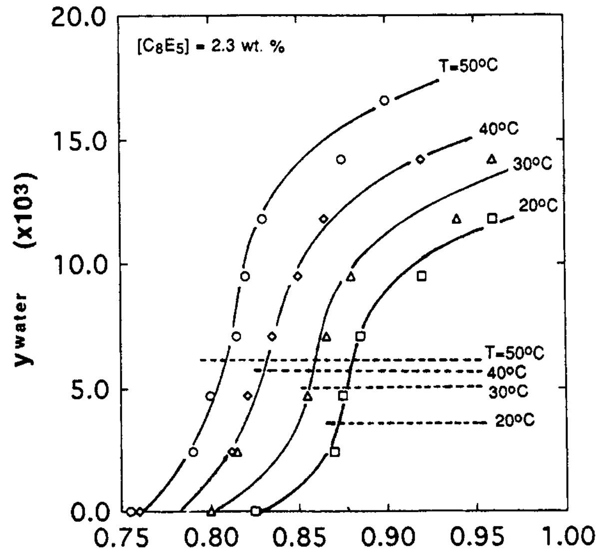

Figure 4. Solubilization of water into C_8E_5 aggregates in CO_2 as a function of temperature and CO_2 density.

The dashed lines are the solubilities of water in pure CO_2.

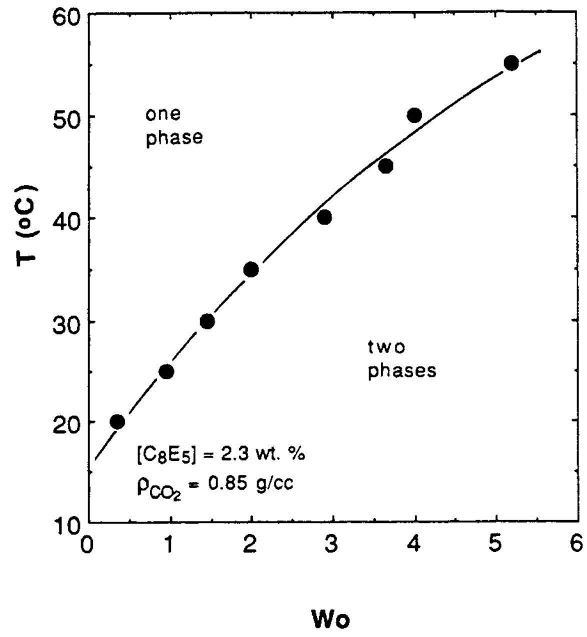

Figure 5. Phase boundary of the C_8E_5/CO_2/water system at a constant CO_2 density of 0.85 g/cm^3.

authors regard the alcohol as a "cosurfactant" which concentrates at the surfactant interface. Some studies suggest that the alcohol operates by inserting itself between surfactant tails and reducing tail-tail and micelle-micelle interactions (Mitchell and Ninham, 1981; Hou and Shah, 1987; Bansal et al., 1980). Other authors have opined that the alcohol acts on the surfactant interface itself, making it more "fluid" and reducing interfacial tension, which promotes the formation of flexible reverse micelles instead of rigid liquid crystalline structures (DeGennes and Taupin, 1982; Asgharian et al., 1991). It is likely that both mechanisms are present, and the predominance of one or the other depends on the particular system. The most effective alcohols have 5-7 carbon atoms, as these alcohols have a polarity intermediate between the hydrophilic short-chain alcohols and the lipophilic long-chain alcohols. Experiments have shown the alcohols to be present at the surfactant interface at a ratio of 2-3 moles of alcohol per mole of surfactant (Petit et al., 1992; DeGennes and Taupin, 1982; Roux et al., 1984; Bansal et al., 1980).

Pentanol was chosen as a cosurfactant for the C_8E_5/CO_2 system, based on its known preference for the surfactant interface and its chain-length compatibility with C_8E_5. Bansal et al. (1980) have suggested that the sum of the chain length of the alcohol and the oil should equal the length of the surfactant tail for the formation of optimal water-in-oil aggregates. Pentanol would fulfill this criterion for a CO_2/C_8E_5 system. Accordingly, solutions of C_8E_5 were made up at a constant wt. % surfactant (on a cosurfactant-free and water-free basis) with various amounts of added pentanol. Water was added by the motor driven injector, and the maximum amount that could be solubilized at 60°C and 345 bar was determined, as shown in Table 1. The "corrected W_o" is adjusted both for the water solubilized in the CO_2 and for the increment associated with pentanol in the bulk CO_2 phase. This latter amount was measured in a separate experiment and found to be very small in comparison to the solubility of water in CO_2—about 0.0089 g H_2O/g pentanol at 60°C and 345 bar.

Table 1 shows that the addition of pentanol leads to significant increases in W_o. On a corrected basis, W_o reaches 12 for a C_8E_5 concentration of 2.5 wt. %. This value is significantly higher than for other surfactants in CO_2 (McFann, 1993; Consani and Smith, 1990). The W_o drops off significantly for surfactant concentrations of 5.0 and 10.0 wt. %. As shown below, this is likely due to increased interactions between aggregates, due to the higher concentration of aggregates. However, the solution with 10.0 wt. % C_8E_5 solubilizes the largest absolute amount of water. This absolute water solubility is higher than has been reported previously for surfactants in CO_2. However, it is still far lower than the water solubilization that can be attained by using nonionic surfactants in liquid alkane solvents (Aveyard et al., 1989; Zhu et al., 1992).

The amounts of pentanol required to solubilize significant amounts of water for C_8E_5 in CO_2 are relatively large, both in terms of the molar ratio of pentanol to C_8E_5 and in comparison to the amounts used in liquid systems to saturate the surfactant interface (Roux et al., 1984; Bansal et al., 1980; Hou and Shah, 1987). The propensity of pentanol to partition to the surfactant interface vs. the lipophilic solvent appears to be lower for CO_2 than for alkane solvents. This difference may be explained by the Lewis acidity and polarity of CO_2 (O'Shea et al., 1991), which strengthen the interactions with the alcohol (Fulton et al., 1991; Yee et al., 1992). Consequently, a much larger overall amount of alcohol in the bulk CO_2 phase is required to achieve a concentration at the surfactant interface high enough for an enhancement of surfactant aggregation and water solubilization.

Solvatochromic probe studies

The shift in the absorbance maximum of a solvatochromic probe is a sensitive measure of the local environment about the probe. Previous studies of solvatochromic shifts for ionic and nonionic surfactants in supercritical ethane provide a basis for the present study (Johnston et al., 1989b; Fulton et al.,

Table 1. Solubilization of Water in C_8E_5 Aggregates in CO_2 with Pentanol Added

mol % C_5OH	$\frac{\text{mol } C_5OH}{\text{mol } C_8E_5}$	W_o, Loaded*	W_o, Corrected	wt. % Water, Loaded
		2.5 wt. % C_8E_5		
0	0	4.0	1.6	0.52
2.0	6	7.0	4.6	0.94
4.0	13	12.0	9.2	1.56
5.8	18	15.0	11.6	1.90
		5.0 wt. % C_8E_5		
0	0	2.0	0.8	0.54
2.2	4	3.5	1.7	0.94
4.4	7	4.0	2.5	1.07
6.3	10	5.5	3.9	1.47
8.2	13	6.0	4.3	1.60
9.9	16	9.0	7.1	2.38
		10.0 wt. % C_8E_5		
0	0	1.4	0.8	0.79
2.2	2	2.8	2.1	1.57
3.4	3	3.7	2.9	2.07
5.8	5	4.2	3.4	2.34
6.7	6	5.1	4.2	2.82
9.0	8	6.5	5.6	3.57
10.5	9	7.4	6.5	4.05

*At 60°C, 345 bar.

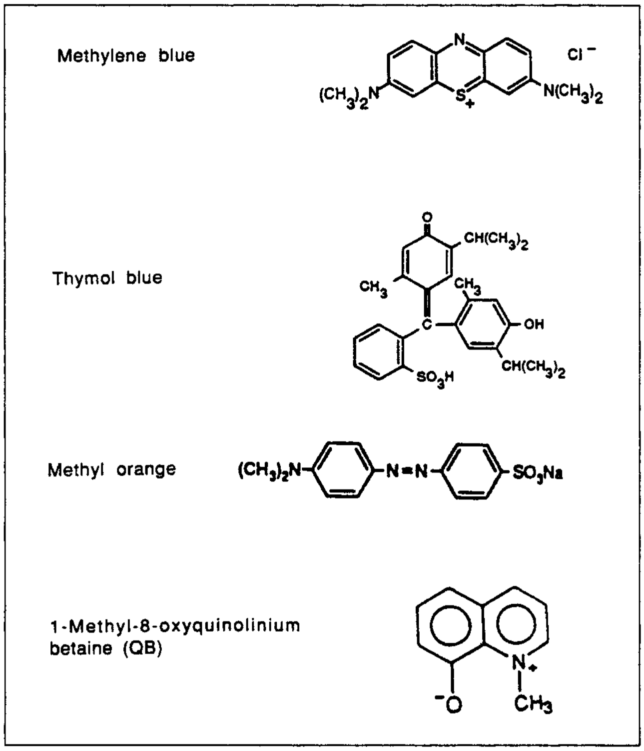

Figure 6. Ionic dyes and solvatochromic probes.

1989; Yazdi et al., 1990). Recently, the solvatochromic dyes methyl orange and 1-methyl-8-oxyquinolinium betaine (QB) (see Figure 6) have been used to investigate the aggregation of the nonionic surfactant Triton X-100 in nonpolar solvents (Zhu and Schelly, 1992; Zhu et al., 1992). The main difference between the two probes is that QB is much smaller and somewhat more hydrophilic than methyl orange. Therefore, QB would be expected to be more strongly attracted to the polar core of a nonionic surfactant reverse micelle. The measured and reported values of λ_{max} of QB are shown in Table 2. It is a blue-shift indicator: λ_{max} moves to shorter wavelengths as the solvent polarity increases. Methyl orange, on the other hand, is a red-shift indicator. The measured λ_{max} of methyl orange in water agrees with the λ_{max} reported by Zhu and Schelly (1992).

The λ_{max} of QB in "dry" aggregates (no added water) of C_8E_5 in CO_2 was measured in the fixed volume UV cell at 40°C (Figure 7). The nominal loading of QB in the cell was 5×10^{-4} M, but only a portion of it was solubilized into the surfactant aggregates based on the measured absorbances. The smallest surfactant concentration at which a λ_{max} could be measured was 4.6 wt. % C_8E_5. For all these data, the C_8E_5 was fully soluble based on visual observation of the UV cell and on the data of Figure 3.

Table 2. UV λ_{max} of QB in Various Solvents

Solvent	Measured λ_{max}, nm	Reported λ_{max}, nm*
water	442.8	443
methanol	466.7	468
butanol	491.6	493
C_4E_2	494.5	—

*From an $E_T(30)$ correlation in Ueda and Schelly (1989).

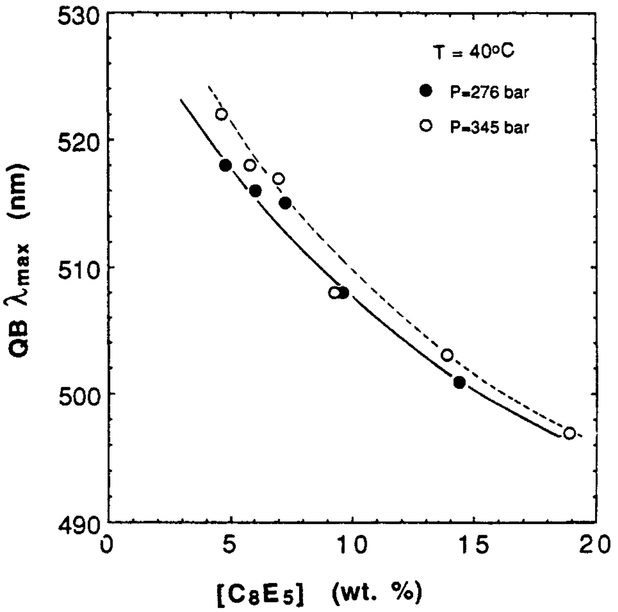

Figure 7. λ_{max} of QB in reverse micelles of C_8E_5 in CO_2 without added water.

Nonionic surfactants aggregate in nonpolar solvents by a stepwise multiple equilibria mechanism, with a gradual increase in the average aggregate size as surfactant concentration increases (Ruckenstein and Nagarajan, 1980; Gelade et al., 1986). Previous studies (Johnston et al., 1989b; Fulton et al., 1991) suggest that the aggregation number decreases with an increase in pressure for nonionic surfactants in supercritical solvents. Both of these trends are evident in Figure 7. As the C_8E_5 concentration increases, the λ_{max} decreases. The highest polarity measured (lowest λ_{max}) is close to that of the pure surfactant C_4E_2 (Table 2), suggesting that the probe is entirely surrounded by surfactant headgroups at higher surfactant concentrations. This would be consistent with the presence of small surfactant aggregates, as a single surfactant headgroup would not be enough to shield the probe molecule from the solvent phase. Thus, this increasing polarity is strong evidence of increasing aggregation of surfactant head groups.

The effects of added water are shown in Figure 8 for a C_8E_5 concentration of 2.3 wt. %, with 8.6 wt. % pentanol as cosurfactant. At $W_o = 0$ the interior polarity of the C_8E_5 aggregates, as indicated by the QB λ_{max}, is already significantly higher than in the case without added pentanol (Figure 7). In fact, very little aggregation occurs for C_8E_5 alone at 2.3 wt. % concentration. Clearly, pentanol promotes aggregation of surfactant. As water is added, the interior polarity reported by QB increases. Studies in liquid systems have shown that the micelle size and aggregation number increase significantly as water is added (Ravey et al., 1984). Thus, the CO_2 system exhibits the expected behavior.

The W_o values in Figure 8 are based on the total amount of water loaded into the cell; some of the water is in the bulk CO_2 phase. Nevertheless, the steady increase in interior polarity with W_o suggests that at least some of the added water partitions into the surfactant and promotes aggregation, as is also suggested by the data of Figure 4. At the phase transition point which occurs at a total W_o of 6, the corrected W_o is 4 based on the solubility of water in CO_2 (Wiebe, 1941).

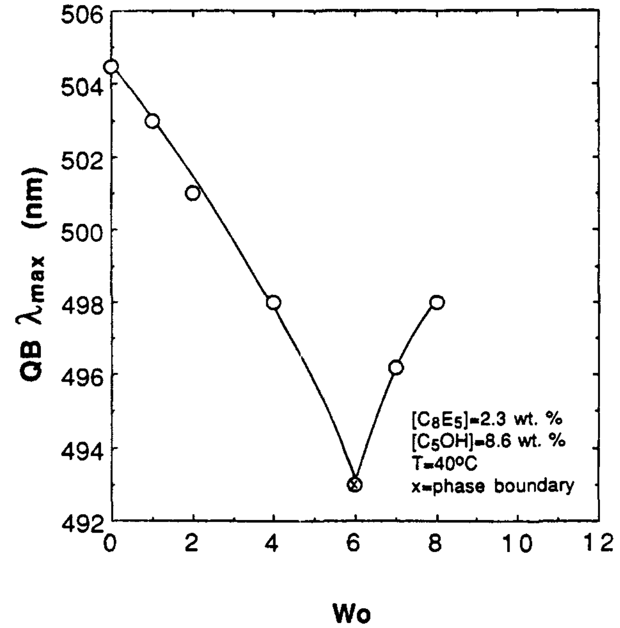

Figure 8. QB λ_{max} in C_8E_5 reverse micelles in CO_2 with pentanol and water added.

For W_o below 6 only one phase is present, whereas at higher values a surfactant rich liquid phase precipitates.

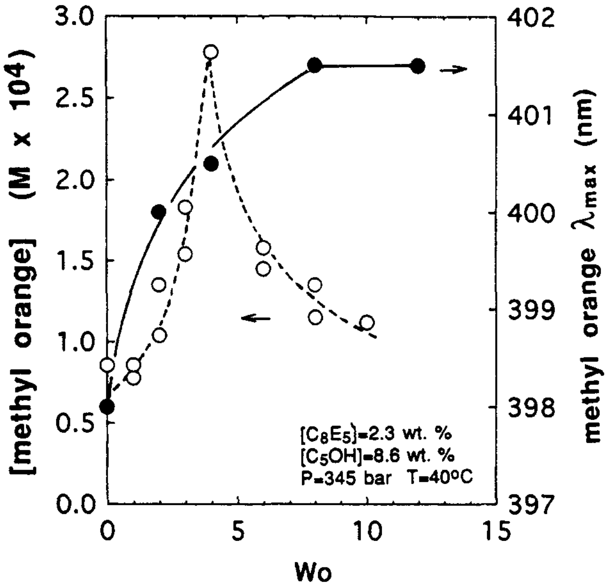

Figure 9. Methyl orange λ_{max} and solubilization in C_8E_5 reverse micelles in CO_2 with water and pentanol added.

At W_os beyond the phase transition point in Figure 8, the QB λ_{max} moves toward a lower polarity, and the QB peaks get much smaller. These changes indicate smaller aggregates with less water in the CO_2 phase. At the same time, precipitated surfactant is clearly visible at the bottom of the UV cell, beneath the beam path. The changes in λ_{max} and peak size, together with the precipitated surfactant, suggest that the phase transition is produced by interactions between the surfactant aggregates. These changes cannot be explained merely by precipitation of excess pure water.

The λ_{max} of methyl orange is shown in Figure 9 for the same composition as in Figure 8. Since methyl orange is a red-shift dye (λ_{max} increases with increasing polarity), the increase in λ_{max} with W_o indicates increasing aggregation. However, the solvatochromic shift of methyl orange does not go through an extremum like that of QB. Methyl orange is considerably less polar than QB, and all of the λ_{max} values report a relatively nonpolar environment. Apparently, methyl orange appears to be excluded from the more polar hydrogen bonding sites by water. This trend continues even beyond the phase boundary where surfactant, water, and dye precipitate, since a few nonpolar solubilization sites remain.

FTIR spectroscopy

FTIR spectroscopy may be used to detect various environments for the water molecules, such as water in bulk CO_2 vs. water in surfactant aggregates. Generally, the characterization of water in a reverse micelle is by observation of shifts in the ν (O-H) stretching mode of water at about 3,500 cm^{-1} (MacDonald et al., 1986). Unfortunately, the absorptions of CO_2 itself obscure these modes. However, it has been suggested (Scheuing, 1990) that shifts in the position of the bending mode may be used to distinguish "bound" and "bulk" water in micelle systems.

In our experiments, FTIR spectroscopy clearly shows the presence of all of the components, C_8E_5, pentanol, and water, in the single CO_2 phase (see Figure 10). A comparison of the bending mode [$\delta(H_2O)$ at about 1,610 cm^{-1}] in these spectra reveals a distinct broadening of the higher frequency side of this band with the addition of C_8E_5 and alcohol. Although this

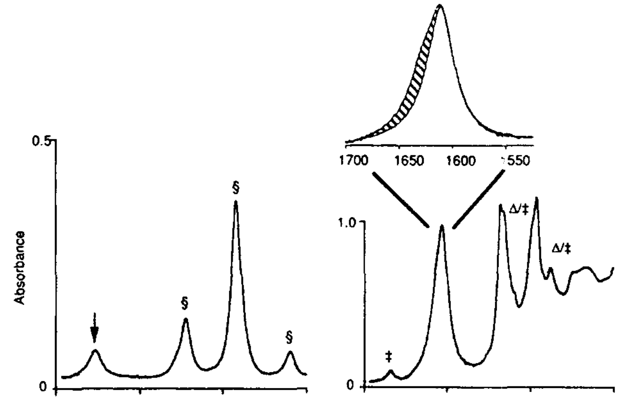

Figure 10. FTIR spectra of a supercritical carbon dioxide solution containing 2.5 wt. % C_8E_5, 6 mol % pentanol, and with a W_o = 10 at 60°C and 5,000 psia.

The spectra show the presence of all the components. In particular, water is identified by the $\delta(H_2O)$ band at about 1,610 cm^{-1} and a weak combination mode (see arrow) about 5,310 cm^{-1}. Other infrared bands are assigned to CO_2 (§), C_8E_5 (‡) and pentanol (Δ). As shown in the inset, a comparison with the $\delta(H_2O)$ band of a saturated water solution at the same temperature and pressure in the absence of C_8E_5 and pentanol clearly reveals broadening of the band in the micellar solution.

Table 3. Dye Solubilization in Nonionic Surfactant Systems

System	[Methylene Blue], M	[Thymol Blue], M	[Methyl Orange], M
heptane	5.0×10^{-7}	5.7×10^{-6}	insol.
heptane + 4 mol % pentanol	7.0×10^{-7}	5.2×10^{-5}	1.0×10^{-8}
5.0 wt. % $C_{12}E_4$ in hexane	7.3×10^{-7}	4.0×10^{-4}	4.2×10^{-5}
5.0 wt. % $C_{12}E_5$ in heptane	2.4×10^{-6}	1.8×10^{-6}	6.7×10^{-6}
5.0 wt. % $C_{12}E_5$ $W_o=1$	1.4×10^{-4}	3.8×10^{-4}	4.2×10^{-4}
5.0 wt. % $C_{12}E_5$ $W_o=5$	4.0×10^{-4}	7.6×10^{-4}	2.0×10^{-4}
5.0 wt. % $C_{12}E_5$ $W_o=10$	4.0×10^{-4}	1.0×10^{-3}	1.0×10^{-4}
CO_2 + 2.3 wt. % C_8E_5 + 8.6 wt. % pentanol @ 40°C, 345 bar	2.3×10^{-5} $(W_o=6)$	—	2.6×10^{-5} $(W_o=4)$

broadening does not provide conclusive spectroscopic evidence for reverse micelle formation, it suggests that surfactant-rich environments are present for water in addition to bulk CO_2, which supports the phase behavior data.

Dye solubilization studies in the C_8E_5/CO_2/water system

Information about the molecular environment in C_8E_5 aggregates in CO_2 can be obtained by comparing solubilities of dyes of varying polarity, in this case, methylene blue, methyl orange and thymol blue. Furthermore, these solubilities may be calibrated with those in liquid systems of known aggregation state. Methylene blue, the most hydrophilic of the three dyes, has been used to identify water-in-oil microemulsion phases (Hou and Shah, 1987; McFann, 1993). Methyl orange is relatively nonpolar and has been used by Zhu and Schelly (1992) to study the aggregation of Triton X-100 in cyclohexane. Thymol blue is of intermediate hydrophilicity. It is a well-known acid-blue indicator used by El Seoud and Shimizu (1982) to define a pH for the interior of AOT reverse micelles. Fulton et al. (1989) used it to probe the interiors of reverse micelles. It is clear from the previous studies that thymol blue is attracted to surfactant interfaces and can be solubilized in a wide variety of systems.

As shown in Table 3, the three dyes are insoluble to sparingly soluble in heptane. The addition of 4 mol % pentanol makes the system slightly more hydrophilic and raises the solubility of thymol blue, which would be expected to prefer an alcohol-like environment. The presence of $C_{12}E_4$, even in its minimal aggregation state without added water, increases the solubilities of thymol blue and methyl orange substantially. The interior polarity of the reverse micelles is sufficient to solubilize these two dyes, but not the most hydrophilic dye methylene blue.

Further experiments were performed with $C_{12}E_5$, which is more hydrophilic than $C_{12}E_4$. In fact, $C_{12}E_5$ does not even dissolve in heptane unless water is added. Thus, the level of dye solubilization in $C_{12}E_5$ at $W_o=0$ (in the heptane phase above the precipitated surfactant phase) is very low. When water is added to increase W_o from 1 to 10, both the aggregate size and interior polarity increase (Ravey et al., 1984). The solubilities of the more hydrophilic dyes, methylene blue and thymol blue increase significantly as expected. The opposite occurs for the least polar dye, methyl orange, which has a smaller affinity for a hydrophilic environment. Water can displace it from ether oxygen sites on the surfactant.

For the C_8E_5/pentanol/H_2O/CO_2 system, the solubilities of the three dyes are intermediate between those for the slightly aggregated $C_{12}E_4$ system and the more aggregated $C_{12}E_5$ system at low W_o. In the case of methyl orange, the solubility in systems composed of CO_2, pentanol and water without C_8E_5 is typically 5.0×10^{-6} M. The addition of 2.3 wt. % C_8E_5 raises the solubility by a factor of 4.5 at 345 bar. As shown in Figure 9, the dye solubility increases to the phase transition point at $W_o=4$. Here, the aggregates grow based on the solvatochromic data (see also Figure 8). As W_o is increased, surfactant precipitates and, consequently, the solubility of dye decreases. For the remaining dye, there is still some aggregation in the CO_2 phase. Indeed, the λ_{max} of the remaining dye continues to increase slightly. These results suggest that C_8E_5 aggregates exist in CO_2, but are quite small.

Effect of pressure

The influence of pressure on dye solubilization was studied for systems composed of CO_2, C_8E_5, water and pentanol, with solid methylene blue (Figure 11) or methyl orange (Figure 12). These ionic dyes are essentially insoluble in CO_2 alone. At all

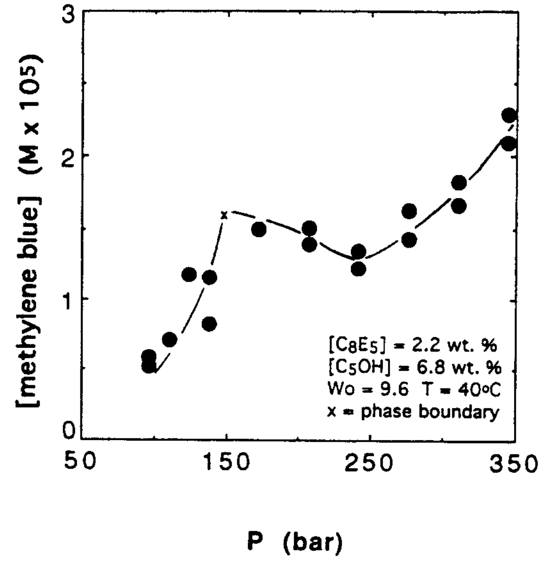

Figure 11. Pressure effects on methylene blue solubilization in C_8E_5 reverse micelles in CO_2.

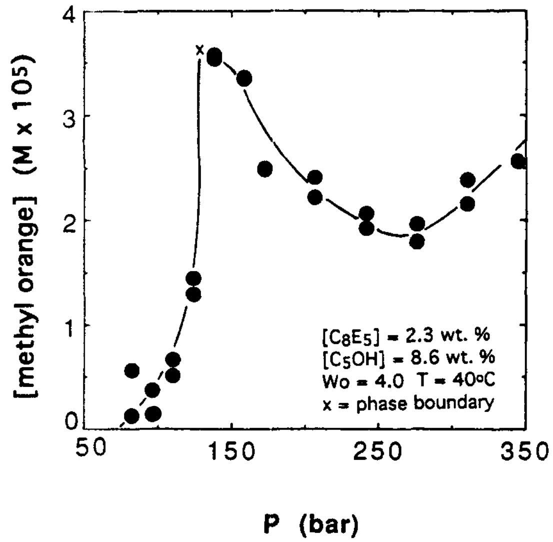

Figure 12. Pressure effects on methyl orange solubilization in C_8E_5 reverse micelles in CO_2.

pressures, there were excess dye particles on the bottom of the view cell, so the surfactant aggregates could be assumed to be saturated with dye. At pressures above the haze point (marked by an x), all of the surfactant, alcohol and water are soluble in CO_2, in equilibrium with excess crystals of dye. The haze point is defined as the point where a new liquid phase precipitates with a decrease in pressure. It is also often called a dew point. In the case of methylene blue, the highest solubilization was found at the highest pressure, 345 bar, a somewhat unexpected result. Increasing pressure is generally thought to break up nonionic surfactant aggregates (Johnston et al., 1989b; Fulton et al., 1990), which would be expected to reduce solubilization. The increase in solubility is not caused by changes in the surfactant solubility, since the surfactant is fully soluble in this region. It is not due to large changes in CO_2's affinity for water, as the solubility of water in CO_2 changes only from 0.0055 to 0.0058 mol fraction between 250 and 350 bar (Wiebe, 1941). Over this range, the 8.5% increase in CO_2 density appears to change the subtle balance of forces at the surfactant interface and induce structural changes in the aggregates, such as the spacing between head groups and the distribution of water (Calderaru et al., 1992). These changes may create more solubilization sites for the dye. Below 250 bar, the solubilization goes through a local minimum and then increases modestly as the haze point is approached at 145 bar. Near the haze point, there are undoubtedly structural changes in the reverse micelles, which create a more favorable environment for the dye. Nonionic surfactant aggregates are known to change size and to undergo micelle-micelle interactions in the neighborhood of phase transitions (Lindman and Wennerstrom, 1991; Fletcher and Holzwarth, 1992; Almgren and Johannsson, 1992). It is also possible that some of the water in the bulk CO_2 phase is attracted to the expanded aggregate clusters and increases their interior polarity in the immediate vicinity of the haze point. Below the haze point, the solubilization drops to zero as the surfactant, cosurfactant, and water precipitate.

The results for methyl orange in Figure 12 are similar to those for methylene blue, except that the changes in solubility immediately above the haze point are more pronounced for the former. Possibly, the growth in the number of solubilization sites caused by micelle-micelle interactions is larger for the less polar dye, methyl orange.

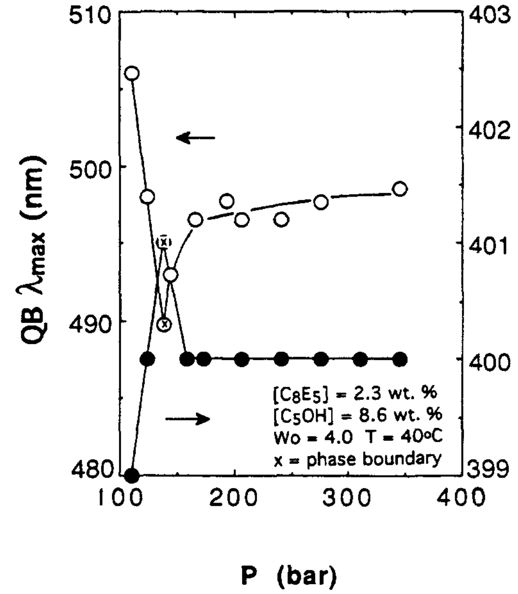

Figure 13. Pressure effects on the λ_{max} of QB and methyl orange in C_8E_5 reverse micelles in CO_2.

At pressures above the phase boundary, only one phase is present.

Pressure effects were also studied by measuring solvatochromic shifts at the same concentration, pressure and temperature conditions as for the above solubility data. These solvatochromic data help clarify the issues raised by the dye solubility data. As shown in Figure 13, the λ_{max} values of methyl orange and of QB are relatively constant at higher pressures. Consequently, the increases in dye solubilization in this region may be caused by conformational changes in the C_8E_5 aggregates that do not change the actual interior polarity very much. For example, changes in the alignment of the surfactant tails with CO_2 density could produce more available sites with the same polarity. There is an abrupt increase in interior polarity close to the haze point, which is consistent with the aggregate growth and clustering phenomenon discussed above. This haze point effect on solubilization and λ_{max} is present for both QB and the much less polar methyl orange. The larger relative change in λ_{max} for QB vs. methyl orange suggests an increase in water content of the aggregate interior, or at least a redistribution of water or probe to the more polar regions of the aggregate. Below the haze point, of course, the interior polarity drops off rapidly due to failure of aggregation, followed by precipitation of water and surfactant.

Nature of the phase transition in C_8E_5/water/oil systems

The phase boundary between one-phase and two-phase C_8E_5/CO_2/water systems could arise from one of the two following mechanisms. In the micelle-micelle interaction mechanism, attractive forces due to overlap between the tails of neighboring reverse micelles cause surfactant and water to precipitate into a new surfactant-rich phase (Roux et al., 1984; Peck and John-

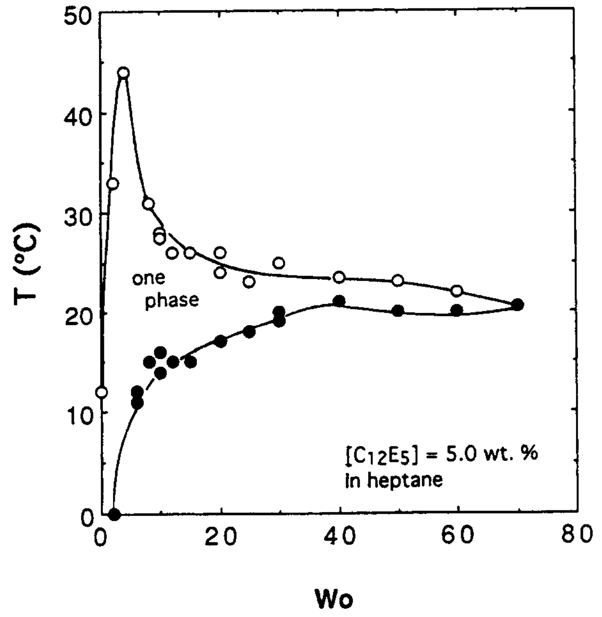

Figure 14. One-phase region of the $C_{12}E_5$/heptane/water system.

Open circles are on the solubilization boundary; closed circles are on the haze point boundary.

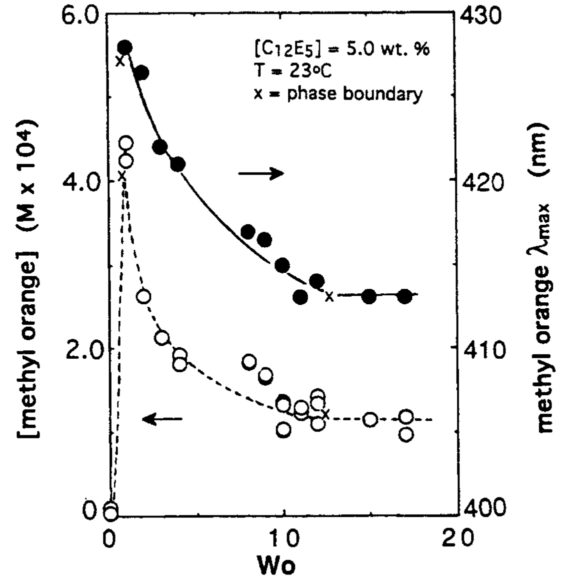

Figure 15. Methyl orange solubilization and λ_{max} in the $C_{12}E_5$/heptane/water system.

ston, 1993). In the natural curvature mechanism, relatively pure excess water precipitates when the micelle radius becomes equal to the natural curvature (Hou and Shah, 1987). The natural curvature corresponds to the radius of a reverse micelle droplet in the absence of interactions between droplets. The roles of these two mechanisms have been investigated for ionic surfactant systems in propane both experimentally (McFann and Johnston, 1991; Yazdi et al., 1991) and theoretically (Peck and Johnston, 1991, 1993). In the case of the C_8E_5/CO_2/water system, the evidence so far, especially in Figure 8, suggests that its phase transitions are caused by micelle-micelle interactions. To confirm this suggestion, we examine the trends in dye solubilization and solvatochromic shifts in conjunction with phase behavior data. To place the CO_2 results in perspective, we begin with an analysis of phase transitions in conventional hydrocarbon solvents.

The one-phase region in a temperature vs. W_o-phase diagram of a nonionic surfactant system in oil extends to large W_o values over a narrow temperature interval (Kon-no and Kitahara, 1970; Aveyard et al., 1989; Hou and Shah, 1987; Shinoda and Ogawa, 1967). An example is shown for the $C_{12}E_5$/heptane/water system in Figure 14. It is well established that the upper boundary of the one-phase region results from the natural curvature mechanism. It is called the solubilization curve, in reference to the solubilization of water. As temperature is increased, water comes out of solution without surfactant. Phase separation at the lower boundary is caused by micelle-micelle interactions. It is usually called the haze point boundary. At temperatures below the haze point boundary, a surfactant-rich and a surfactant-lean phase are present. At a fixed temperature, a reverse micelle system would be expected to display strikingly different trends in dye solubilization and solvatochromic behavior vs. W_o at the haze point vs. solubilization-phase boundary.

In Figure 14, the upper phase boundary is crossed twice at 25°C, first at $W_o=1$ and again at $W_o=20$. The latter phase boundary is clearly governed by the natural curvature mechanism. Even though the $W_o=1$ boundary is also on the solubilization curve, it actually represents the onset of aggregation at low W_o, as revealed by the dye solubilization data of Table 3. A small amount of water facilitates the aggregation. Thus, it is more analogous to a micelle-micelle interaction boundary.

The solubilization and λ_{max} of methyl orange are shown for the $C_{12}E_5$/heptane/water system in Figure 15. This same system is also shown in Table 3. Visual observation of the phase behavior, the λ_{max} values, and the dye solubilization all show a phase transition point at $W_o=12$, rather than $W_o=20$, as was indicated in Figure 14. This variation may be caused by the perturbing influence of the ionic dye. In the one-phase region between $W_o=1$ and $W_o=12$, the methyl orange solubility and λ_{max} steadily decrease, indicating a decrease in the polarity of the surroundings for the probe in the reverse micelles. At the onset of aggregation at $W_o=1$, the reverse micelles are probably loosely organized and not very polar. As above, a small amount of water raises solubility and facilitates aggregation. Methyl orange penetrates to the center of such aggregates and finds a compatible polarity. However, as water is added, it gathers at the center of the reverse micellar structure, near the -OH terminus of the ethylene oxide chains (Caldararu et al., 1992). The methyl orange is gradually forced into the regions of lower polarity near the hydrocarbon end of the ethylene oxide chain, as indicated by λ_{max}. Since these sites are less favorable for solubilization, the concentration of methyl orange in the overall system decreases right up to the natural curvature phase boundary at $W_o=12$. At higher values of W_o in the two-phase region, the methyl orange λ_{max} and solubilization reach a plateau, since the reverse micelle size and interfacial curvature remain constant.

A different type of behavior is seen in the Triton X-100 system in a 70/30 (v/v) mixture of hexane and benzene. The system contains 22.1 wt. % Triton X-100 at $W_o=0$, which is

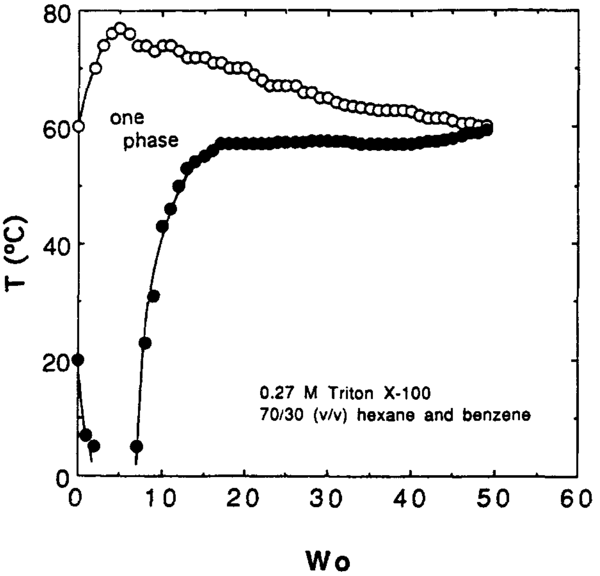

Figure 16. One-phase region of the Triton X-100 system in a 70/30 (v/v) mixture of hexane and benzene.

Open circles are on the solubilization boundary, closed circles are on the haze point boundary.

equivalent to the 0.27-M concentration used by Zhu et al. (1992). In this system, the solubilization phase boundary lies well above room temperature, as shown in Figure 16. Thus, it is the haze point curve rather than the solubilization curve that is crossed at 25°C. The λ_{max} (Zhu et al., 1992) is plotted with new methyl orange solubility data in Figure 17. Up to $W_o = 7$, the methyl orange solubilization and λ_{max} both increase with W_0. Here, the reverse micelles grow and become more polar with added water up to the micelle-micelle interaction boundary. The growth increases the number of solubilization sites, so solubility of dye increases. The phase boundary itself was observed at $W_o = 8$, near the reported value of 9 (Zhu et al., 1992). Again, the dye may perturb the system. In the two-phase region, the water and surfactant precipitate, decreasing the solubilization of the dye. As the haze point is approached, the changes in reverse micelle polarity and dye solubilization are identical to those seen in Figures 9, 11 and 12 in CO_2. Thus, the phase transition at the haze point is caused by the same mechanism, that is micelle-micelle interactions in both cases.

Comparison of results in CO_2 and liquid alkanes

Let us return to the $C_8E_5/CO_2/H_2O$ system in Figure 5 for a constant CO_2 density of 0.85 g/cm^3. The boundary between the one-phase and two-phase regions resembles the lower temperature curve of the Triton X-100 system of Figure 16. The trends in methyl orange solubilization and λ_{max} for C_8E_5 in CO_2 (Figure 9) are very similar to those for the Triton X-100 system in Figure 17. Thus, it can be concluded that the phase separation (haze point) in the $C_8E_5/CO_2/H_2O$ system is governed by micelle-micelle interactions at the conditions studied. These results indicate that pressure may be used as another variable in addition to temperature and W_o to effect phase

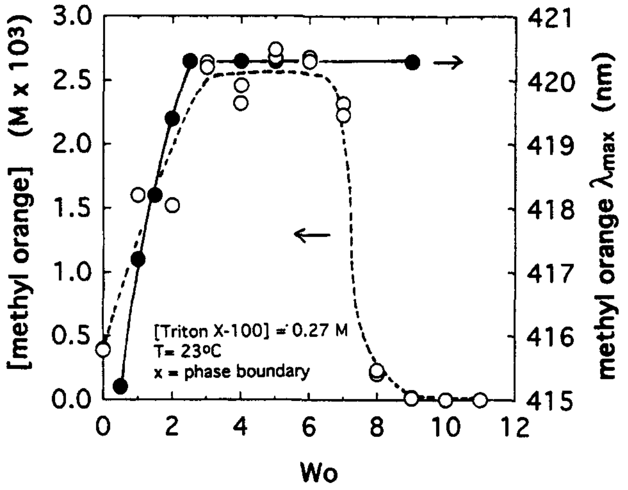

Figure 17. Methyl orange solubilization and λ_{max} in the Triton X-100 system.

separation at the haze point. The region of larger W_0s, if it exists, evidently lies at higher temperatures than those that were studied. At such a temperature, however, pressures as high as 1 kbar would be required to maintain the CO_2 density at 0.85 g/cm^3.

Conclusions

Compared with previously studied nonionic surfactants, C_8E_5 offers the best results with regard to solubility in CO_2 and solubilization of water. The tail length is shorter than the optimum value for liquid alkane solvents because of the low cohesive energy density of CO_2. For this reduced tail length, more EO groups must be present than usual to promote polar interactions which favor aggregation and water uptake. Solvatochromic probe studies show that C_8E_5, without added water, gradually forms small aggregates in supercritical CO_2 as its concentration increases. These aggregates take up very little water. When the cosurfactant pentanol is added, the W_o, corrected for the appreciable solubility of water in pure CO_2, reaches values as high as 12. The FTIR spectra indicate that some of the water is associated with surfactant and cosurfactant, which is distinguishible from water in bulk CO_2. When the W_o is increased still further, the $C_8E_5/CO_2/H_2O$ system forms two phases due to micelle-micelle interactions. In the one-phase region, the probes QB and methyl orange both show increases in the interior polarity of the C_8E_5 aggregates as water is added. The aggregates can solubilize ionic dyes such as methyl orange, methylene blue, and thymol blue, which are insoluble in CO_2 alone. Both dye solubilization and solvatochromic probe data show significant changes near the phase boundary as the size and structure of the aggregates change with pressure. A comparison of these C_8E_5 systems in CO_2 with nonionic surfactant systems of known behavior in liquid hydrocarbon solvents show that the aggregates formed in CO_2 are significantly smaller. To form larger aggregates in CO_2 future work should be performed with nonionic surfactants and cosurfactants as in this study or with new types of surfactants that have tails with lower cohesive energy densities (Hoefling et al., 1991).

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