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INTERFACIAL PHENOMENA AT THE COMPRESSED CO_2-WATER INTERFACE

B. Bharatwaj and S. R. P. Rocha*

Chemical Engineering and Materials Science,
Wayne State University, Detroit, MI 48202, USA.
E-mail: sdr@eng.wayne.edu

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Abstract - Compressed CO_2 is considered to be a viable alternative to toxic volatile organic solvents with potential applications in areas including separation reactions, and materials formation processes. Thus an interest in CO_2 stems from the fact that it is very inexpensive, has low toxicity, and is not a regulated. However, compressed CO_2 has a zero dipole moment and weak van der Waals forces and thus is a poor solvent for both polar and most high molecular weight solutes, characteristics that severely restrict its applicability. In order to overcome this inherent inability, surfactant-stabilized organic and aqueous dispersions in CO_2 have been proposed. This work will discuss fundamentals and recent advances in the design of amphiphiles for the novel CO_2-water interface.

Keywords: High pressure; Interfacial tension; Surfactants; Water-in-CO_2 microemulsions.

INTRODUCTION

Development of energy-efficient and “green” alternatives to conventional separation and materials formation processes are keys to economical development in times of uncertainties in the world petroleum market and of tighter environmental regulations. CO_2 is cheap, is not regulated by either the FDA or EPA, has tunable solvent strength, and can be easily recycled. Such unique properties make compressed CO_2 one of the most promising substitutes for toxic and volatile organic solvents. Significant advances in CO_2-based technologies, with applications in areas including the microelectronic industry (Deyoung, *et al.*, 2002), bioseparations (Ghenciu, *et al.*, 1998), and nanoparticle synthesis (Shah, *et al.*, 2003), have been propelled by the discovery of amphiphiles capable of forming and stabilizing colloidal dispersions in compressed CO_2. Despite the progress achieved in the design of polymeric amphiphiles, very little has been done in developing small molecule surfactants that are capable of efficiently stabilizing water-dispersed domains in CO_2, and yet are environmentally friendly and inexpensive (Eastoe, *et al.*, 2003). Current limitations are the small number (mostly fluorinated) of molecules with significant interfacial activity at the CO_2-water (C|W) interface and the generally high pressures required to stabilize formulations involving water and compressed CO_2. The properties of the C|W interface are strikingly different from those of conventional oil-water (O|W) interfaces. Most marked, are (1) the much lower surfactant requirement at the onset of formation of reverse aggregates of water-in-CO_2 (W/C), than that in O|W systems (da Rocha, *et al.*, 2000) and (2) the fact that subtle changes in surfactant chemistry have a profound effect on the pressure required to stabilize the reverse aggregates (Eastoe, *et al.*, 2000, Steytler, *et al.*, 2001). Figure 1 is an idealized picture of W/C reverse microemulsions.

New paradigms have correlated surfactant structure with its activity at the C|W interface. Surfactants with a lower surface tension at the

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*To whom correspondence should be addressed critical aggregation concentration (cac) at the air-water (A|W) interface seem to be more interfacially active at the C|W interface (Eastoe, *et al.*, 2002), than those that provide a large free fractional volume accessible to CO_2 in the monolayer region (da Rocha, *et al.*, 2003, Stone, *et al.*, 2004). A detailed knowledge of the macroscopic properties and molecular level details of the binary and surfactant modified C|W interface is essential to explain these paradigms, thus providing a rational and intuitive framework for surfactant design. These steps are required for the advancement of CO_2-based technology. It is the focus of this work to illustrate how complementary information obtained from experiments and atomistic computer simulations can be used to gain this fundamental understanding of the C|W interface. First, a brief overview of the stability of reverse microemulsions will be presented.

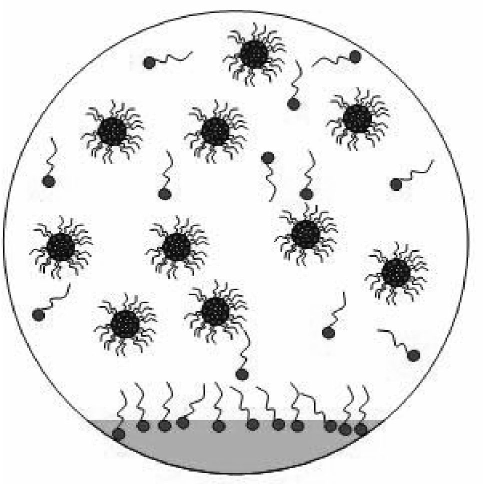

Figure 1: Schematic diagram of a surfactant-stabilized water-in-CO_2 reverse microemulsion in equilibrium with excess water.

MICROEMULSION STABILITY

Instability in water-in-oil (W/O) microemulsions, as indicated by phase separation, can be induced by (1) curvature or (2) attractive droplet interactions (Hou, *et al.*, 1987). Curvature effects arise due to the difference in surfactant head group - head group, and tail-tail interactions, which are mediated by the environment in which they are solvated (Israelachvili, 1994, Israelachvili, 1997). From this difference in interaction, an interfacial bending stress arises on the flat oil-water film, causing it to curve spontaneously to an optimal curvature of $1/R^0$, provided very low interfacial tensions (γ) can be attained. Phase separation will occur when water droplets assume a radius larger than R^0 (will "squeeze out" water molecules). W/O microemulsions and excess water will then be in equilibrium. On the other hand, phase separation due to attractive droplet interactions results in the coexistence of two microemulsion phases of the same curvature. Such attractive interactions arise predominantly due to surfactant tail-tail interactions during microemulsion contact, and to a lesser extent, to the attraction of the water droplet cores (Hou, *et al.*, 1988). The same behavior has been documented for W/C microemulsions (Lee, *et al.*, 2001, McFann, *et al.*, 1994).

Obviously, the relative strength of tail-tail, oil-oil (CO_2-CO_2) and oil-tail (CO_2-tail) interactions will dictate the magnitude of attraction upon collision i.e., whether the microemulsion system is stable or not. In the case of compressible solvents, these interactions will also dictate the minimum pressure required to stabilize such dispersions. Also, the presence of additives such as alcohols (cosurfactants) at the interfacial surfactant film can reduce tail-tail, and thus micelle-micelle, interactions (McFann, *et al.*, 1994). A similar effect is expected with bulkier, more branched surfactant tails (Hou, *et al.*, 1987, Huang, *et al.*, 1984, McFann, *et al.*, 1994), as illustrated in Figure 2. The addition of salt can also reduce intramicellar head-group repulsion (Aveyard, *et al.*, 1986) in a way that tail penetration between interacting droplets is reduced due to greater steric hindrance in the interfacial region.

Even though far from optimized, several successful approaches to the C|W interface have found issues regarding surfactant geometry, i.e., in the ability to bend around water (Eastoe, *et al.*, 2000, Johnston, *et al.*, 1996, Zielinsky, *et al.*, 1997).

Many amphiphiles have also been shown to have an appropriate balance, as revealed by the decrease in the interfacial tension at the C|W interface ($\gamma_{C|W}$)(da Rocha, *et al.*, 1999). However, W/C microemulsions have much stronger attractive interactions than their W/O counterparts, a fact that has been attributed to the enhanced strength of attractive tail-tail interactions between approaching microemulsion droplets (Lee, *et al.*, 2001), which is directly manifested by the high pressures generally required for their stabilization. Therefore, a microscopic level description of the monolayer region along with knowledge of the effect of thermodynamic variables on adsorption of the amphiphiles at interface are essential in the development of inexpensive and environmentally acceptable amphiphiles with high activity at the C|W interface, and yet the ability to stabilize the system at low pressures.

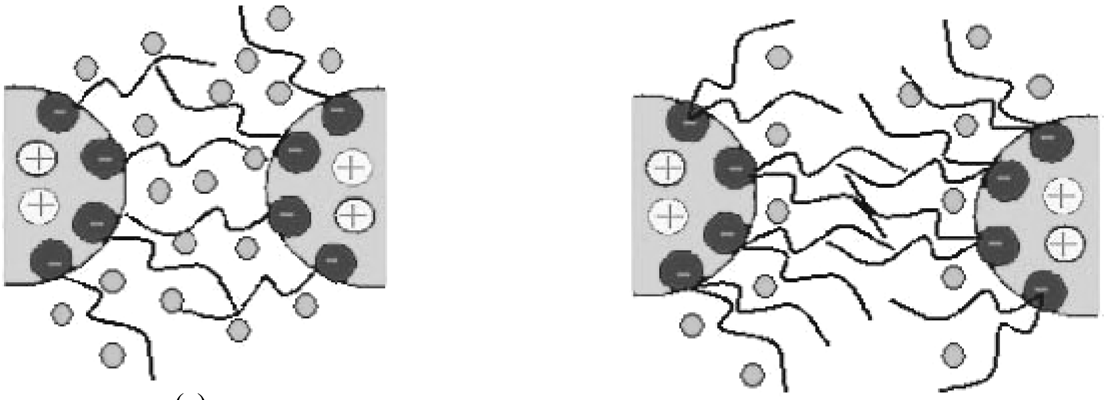
(a) (b)

Figure 2: Schematic diagram of the effect of surfactant coverage on tail-tail interaction in water-in-CO_2 microemulsions. The more crowded interface (*b*), in this case due to the presence of a double-tail amphiphile, evidently prevents more intimate contact between segments of tail groups of surfactants adsorbed at the interface of approaching microemulsion droplets.

MICROSCOPIC INFORMATION ON MONOLAYERS AT THE CO_2-WATER INTERFACE

The microstructure of W/C microemulsions has been the focus of several recent studies using both small angle neutron (SANS) (Eastoe, *et al.*, 2000, Lee, *et al.*, 2001, Zielinsky, *et al.*, 1997) and x-ray (SAXS) (Liu, *et al.*, 2002) scattering. Apart from a more recent study reporting the attractive interaction between microemulsion droplets and an estimate of the thickness of the surfactant monolayer based on an ad-hoc model (Lee, *et al.*, 2001), most of the previous work is focused on the size and surfactant coverage of these droplets (Eastoe, *et al.*, 1997, Lee Jr., *et al.*, 2000). In spite of the widespread interest in the effect of surfactant chemistry on the formation and stability of these aggregates, no systematic research on the microscopic properties of surfactant monolayers at the C|W interface has yet been reported.

Powered by recent advances in computer algorithms and fast and inexpensive computers, results from molecular dynamics (MD) computer simulations have filled some of the gaps left by previous experimental approaches, and have also helped to support some of the previously proposed paradigms. Insight into the microstructure of the bare and surfactant modified C|W interfacial region was recently reported (da Rocha, *et al.*, 2001, 2002, 2004, Salaniwal, *et al.*, 2001, Senapati, *et al.*, 2002, Stone, *et al.*, 2003, 2004). Figure 3 is a snapshot of an equilibrium configuration of a perfluoropolyether ammonium carboxylate ($CF_3(OCF_2CF(CF_3))_3OCF_2COO^- NH_4^+$) ($PFPE\text{-}COO\text{-}NH_4^+$) surfactant at the C|W interface (da Rocha, *et al.*, 2002) obtained by MD computer simulations. The significant penetration of CO_2 into the monolayer region can be qualitatively observed. This important feature is shown in quantitative detail in Figure 4, where the atomic density profile is given, under the same thermodynamic conditions as in Figure 3. To a large extent, the features observed for amphiphiles at conventional O|W interfaces is preserved for surfactants at the C|W interface. The surfactant head group is completely submerged and well solvated in the aqueous-rich phase, while the surfactant tail group is mostly excluded from the aqueous phase. It is also obvious that CO_2 is capable of penetrating the surfactant tail region to a large extent. At the peak of the fluorine density distribution, the density of CO_2 is approximately 50 % of its bulk value. This is surprisingly greater than that observed for CCl_4 in the hydrocarbon tail region of SDS surfactant at the

CCl_4|W interface (Dominguez, *et al.*, 2000). It should be noted that such a large penetration does not arise due to the low surfactant coverage at the C|W interface (84 $Å^2$/molecule in that case). The generally observed low surfactant coverage at the C|W interface is a direct consequence of the small difference in free energy density difference for the binary C|W interface i.e., a lower surfactant requirement for aggregate formation is driven by the lower interfacial tension of the bare C|W interface (da Rocha, *et al.*, 2000). Another very relevant microscopic insight into the structure-function relationship of surfactants at the C|W interface was provided in a recent MD study of the effect of fluorination of double-tailed phosphate surfactants (Stone, *et al.*, 2003). It was determined that the enhanced activity of *F* amphiphiles at the C|W interface can be correlated with a greater separation of both CO_2 and water from the interfacial region than for its hydrogenated counterpart. This in turn is attributed to both the bulkiness and the enhanced hydrophobicity of *F* atoms.

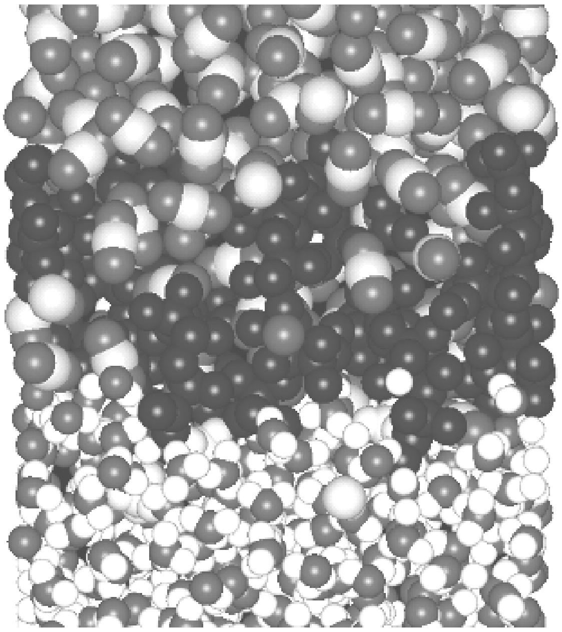

Figure 3: Snapshot of an equilibrium configuration for the interfacial region of the PFPE-COO^- NH_4^+ surfactant at the CO_2-water interface at 318.15 K and average pressure of 23 MPa, obtained by MD simulations. For better visualization, a close-up of the interfacial region is shown (da Rocha, *et al.*, 2002). Surfactant anion is color-coded dark blue, counterion light blue. CO_2 is shown in the upper phase and water in the lower phase.

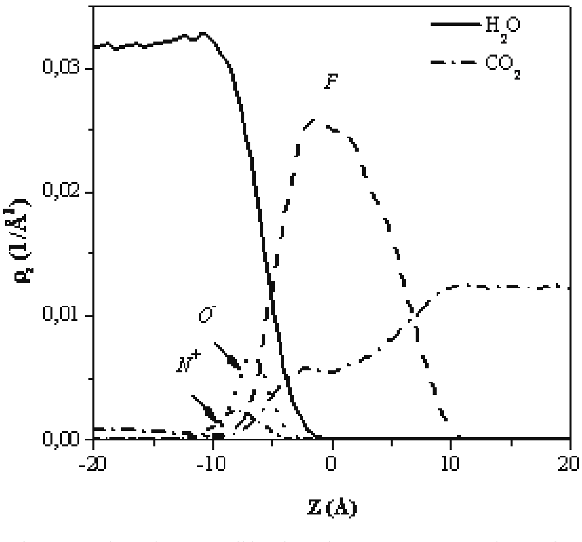

Figure 4: Z-dependent center of mass density profile for the CO_2-water interface at 318.15 K. The surfactant tail group is represented by the fluorine (*F*) profile, while the head group and counterion are represented by the carboxylate oxygen (O^-) and the nitrogen (N^+) density distribution, respectively (da Rocha, *et al.*, 2000, 2002).

While for the most part there seems to be a consensus regarding the use of detailed models for both solvents (water and CO_2), few research projects employ fully atomistic models to describe the chemistry of the surfactant (da Rocha, *et al.*, 2002, Stone, *et al.*, 2004). This is a surprising observation given the significant impact that subtle changes in surfactant architecture have on surfactant activity at the C|W interface (Eastoe, *et al.*, 2000, 2003, Steytler, *et al.*, 2001). For example, substituting a single atom in the surfactant tail terminal group CF_3 to form CHF_2 in a double-tailed semi-fluorinated sulfosuccinate amphiphile requires an increase in pressure of approximately 9 MPa to stabilize a W/C microemulsion with a molar water/surfactant ratio of 10 (Eastoe, *et al.*, 2000). Evidently, such fine details cannot be modeled using a united atom approach. Moreover, united atom models do not account for the significant interaction between the CO_2 quadrupole moment and the surfactant tail-group local dipoles. This interaction plays an essential role in the solvation of species in CO_2 and is therefore expected to significantly affect the overall monolayer organization (da Rocha, *et al.*, 2004). It is also known from experimental observation that replacing the sulfosuccinate surfactant head group by phosphate, as the tail group is kept constant, has the effect of reducing the pressure required to stabilize a W/C microemulsion of about 10 MPa. This observation (Steytler, *et al.*, 2001) clearly illustrates the relevance of a correct model description of the solvation of the head group, as well as the CO_2-philic tail. A fully atomistic description of the surfactant is therefore essential for obtaining the correct physics of the problem.

INTERFACIAL THERMODYNAMICS

Interfacial tension (γ), a direct measure of the surfactant affinity for the interface, and surface coverage (Γ) are the most fundamental properties of amphiphiles at fluid-fluid interfaces. These properties have been determined using the pendant drop technique, adapted to high-pressure systems (da Rocha, *et al.*, 1999). The area occupied per surfactant molecule at the interface $\mathcal{A}$ (=1/Γ) can be calculated with the help of the Gibbs-Adsorption equation:

$$d\gamma = -\Gamma\, RT\, d\ln[c_s]$$

which relates γ to Γ (or $\mathcal{A}$) (da Rocha, *et al.*, 2000). In practice, $\mathcal{A}$ is obtained from the slope of the curve of γ vs. surfactant concentration ([c_s]), before the break in the curve observed as [c_s] increases (Figure 5). The concentration at the break is assigned as the critical aggregation concentration (*cac*) i.e., *cac* delimits the region where the surfactant is molecular solubilized at [c_s] < *cac* and the region where micellar aggregates are formed at [c_s] > *cac*. These definitions are better illustrated in Figure 5.

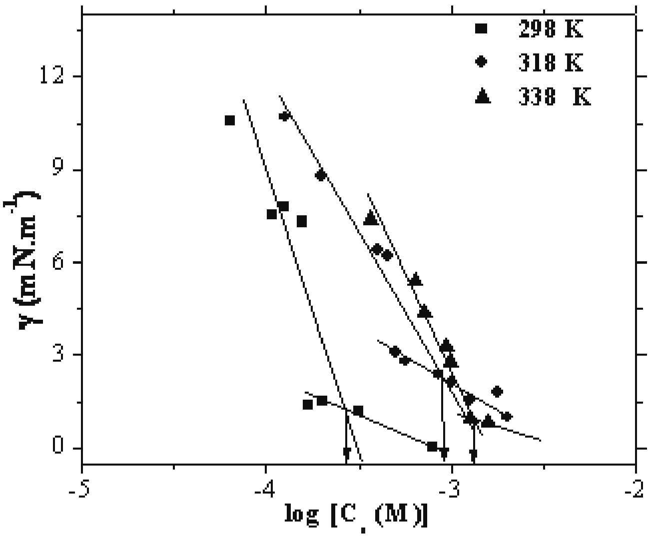

Figure 5: Interfacial tension vs. surfactant concentration [c_s] for a surfactant at the CO_2-water interface. Data sourced from da Rocha et al., 1999 using WinDig software (da Rocha, *et al.*, 1999). The [c_s] indicated by the arrows is the critical aggregation concentration (*cac*). The slope before *cac* is related to Γ, as shown in equation 1 (da Rocha, *et al.*, 2000).

The γ of the C|W interface ($\gamma_{C|W}$) at moderate pressures is ~ 20 mN/m (da Rocha, *et al.*, 1999). The value of ~ 50 mN/m which is much lower than those generally observed in conventional O|W systems(Freitas, *et al.*, 1997), dictates the much lower surfactant requirement for the C|W interface i.e. the large A at the onset of aggregation (da Rocha, *et al.*, 2000). The values of A obtained from Figure 5 for a PFPE-$COO^{-}NH_4^{+}$ 2500MW range from 76 to 107 $Å^2$/molecule as T varies from 25 (liquid) to 65 ^{o}C (supercritical) at a constant solvent power (density) of 0.842 g.ml^{-1}. The free energy ($\Delta G_{\mu ic}$) for microemulsion formation can be calculated from the *cac* values. The associated enthalpy and entropy can also be calculated, providing a detailed description of the thermodynamics of aggregation. These results can be utilized to guide the design of efficient amphiphiles for this interface (da Rocha, *et al.*, 2000). The $\Delta G_{\mu ic}$ observed, is larger than that expected for dipole-dipole interactions (head group-head group), thus reflecting hydrogen bonding of water to the anions and ion hydration. Water molecules can bridge the head groups through hydrogen bonding to form nuclei for further aggregation. Interactions between the ionic head groups and water are thus responsible for the enthalpically driven aggregation process. The enthalpic interactions overcome the unfavorable ordering of the surfactants in the interfacial region (loss of entropy).

SUMMARY STATEMENT AND OUTLOOK

CO_2-based technologies have the potential to replace existing processes where either a significant amount of natural resources are wasted (e.g. water) and/or toxic organic solvents are emitted. Tougher environmental regulations worldwide are expected to provide necessary incentives to pursue such environmentally friendly technologies. It is likely that colloidal-based phenomena will continue to provide innovative routes for the development of new processes utilizing compressed CO_2. However, several issues regarding surfactant design need to be addressed. Most striking is the need for new classes of amphiphiles that are at the same time highly active and inexpensive. A recent study demonstrated the ability to disperse significant amounts of water with a commercial nonionic branched hydrocarbon surfactant (Ryoo, *et al.*, 2003). Methylation and branching of surfactant tails were shown to enhance the formation of stable W/C microemulsions by increasing surfactant solubility in CO_2, shifting the curvature toward bending around water, and finally reducing overlap between surfactant tails and weakening interdroplet interactions. However, the number of water-surfactant (*Wo*) molecules, in this case per head-group repeat unit, is much smaller than what has been obtained for fluorinated surfactants. Equally important is the reduction in the pressure required for stabilization of the aggregates. Subtle changes in the surfactant architecture have been shown to cause very significant reductions in the pressure required for stabilization of reverse microemulsions of water in CO_2 (Eastoe, *et al.*, 2000, Steytler, *et al.*, 2001). Similar success has not been reported for hydrogenated surfactants.

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