

Designing Smart Surfactants

Surfactants and emulsions are used extensively in industrial processes with applications ranging from the petroleum industry to pharmaceuticals. Surfactants are particularly attractive for reactions when compartmentalization or stabilization of reactants and/or products yields control of the size, morphology, or some other property. The largest synthetic use of surfactants is emulsion polymerization, in which surfactants (via micelle formation) efficiently control molecular weight and molecular weight distribution¹. Many commercial polymers are prepared via emulsion polymerization; for example, poly(tetrafluoroethylene) (PTFE or Teflon®), poly(vinylchloride) (PVC), acrylonitrile benzyl styrene (ABS), poly(methylmethacrylate) (PMMA), poly(acrylamide). In these instances the micelles prolong the solubility of growing polymers to yield high molecular weights and relatively few nucleation sites, while the continuous phase provides a low-viscosity medium for rapid heat transfer and monomer diffusion.

In most applications the surfactant is used to enhance stability or reduce heat and mass transport limitations, but rarely is an integral component of the final product. In these cases, surfactant removal and the breaking of the emulsion usually entails addition of heat, mechanical agitation, or chemical interfacial modification with the addition of an emulsion neutralizing agent. These treatments are not only costly; they often lead to product contamination and produce large volumes of surfactant-contaminated aqueous wastes. One solution that has been adopted is the use of “environmentally friendly” or biodegradable surfactants that are disposed of with aqueous waste—at least eliminating the remediation cost. This approach is questionable as far as the environmental impacts and has been targeted by environmental groups as a leading source of water-borne pollution.

In recent years cleavable surfactants, switchable molecules that will “turn off” their surfactant character, have sparked interest in a variety of emulsion-based applications. Cleavable surfactants are attractive for both economic and environmental considerations. Upon the surfactant decomposition, the emulsion is broken and is incapable of reforming, as opposed to thermodynamic breaking which can reform. In the late sixties, Distler² patented a vinyl sulfonate that displayed surfactant properties under acidic conditions and none under basic conditions. Since then, others have developed cleavable surfactants and studied their surface tension effects, micellization, and decomposition. A range of possible “switches” for the decomposition have been investigated: pH³⁻⁶, ozone⁷, ultraviolet light⁸⁻¹², and heat^{13,14}. All have been used to cleave the polar head from the non-polar tail. Unfortunately, an aqueous soluble fragment is always formed from the decomposition, clearly limiting their potential.

Ideally, a surfactant would have specific properties which include:

- The ability to create an emulsion that would facilitate the reaction, by contacting immiscible phases or otherwise overcoming transport limitations.
- Containing a controllable, non-energy intensive switch to suppress or eliminate surfactant activity.
- The surfactant decomposition products would be inert and easily recoverable, existing as a gas or non-ionic hydrophobic species.

- The surfactant would be reversible, where the surfactant decomposition products could be reconstituted into the original surfactant for reuse

A variety of multidisciplinary characterization techniques including spectroscopy, thermal analysis, and neutron scattering are being used to gain a better understanding of these systems and their decomposition mechanisms, as well as potential applications.

Thiirane Oxide Switch

Thiirane oxide is a cyclic analog to DMSO and exhibits similar solvent properties. Unlike DMSO, thiirane oxide undergoes thermal decomposition at temperatures above 100 °C to form ethylene and sulfur monoxide^{15,16} as shown in **Error! Reference source not found.1**. Herein lie the unique properties of thiirane oxide: first, it allows a switch in polarity from a DMSO analog to a small unsaturated hydrocarbon: second, the solvent can be eliminated under moderate conditions for easy product isolation. The aim of this work is to demonstrate the concept of “switchable” or “smart” solvents which combine high reaction performances with easy separation upon application of an external stimulus.

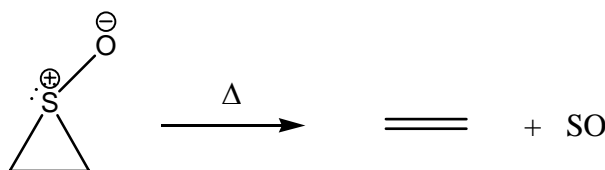


Figure 1. Decomposition of thiirane oxide to ethylene and sulfur monoxide.

Thiirane oxide is reported in the literature and can be easily synthesized from ethylene sulfide¹⁷. Although there is some mechanistic controversy, the decomposition of thiirane oxide is believed to occur via a cheletropic mechanism which extrudes one molecule of SO and one molecule of ethylene. By the principle of microscopic reversibility, the back-reaction, to reform thiirane oxide is possible. However, the rapid disproportionation of SO¹⁸ potentially renders the solvent reformation reaction impractical.

However, we can use the thiirane oxide decomposition as a switch for a smart surfactant. N-octylthiirane oxide has been reported in the literature^{19,20}; but its properties and use as a surfactant have not been studied. Synthesis of n-octylthiirane oxide involves the oxidation of 1-decene to form 1-decylepoide which is then reacted with sodium thiocyanate to yield 1-decylepisulfide. The product is oxidized to form n-octylthiirane oxide (Figure 2). Purification is carried out on a silica gel column resulting in 35% isolated yield (from the 1-decene). Characterization included ¹H and ¹³C NMR, MS, IR Spectroscopy and Elemental Analysis

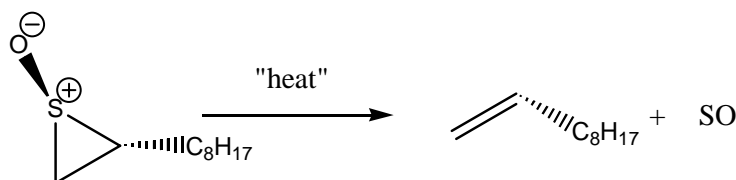


Figure 2. Decomposition n-octylthiirane oxide to 1-decene and sulfur monoxide

The n-octylthiirane oxide is expected to be a thermally labile surfactant—by means of the thiirane oxide head-group—and preliminary investigations have studied its surfactant properties and decomposition. Perhaps the most important is that upon decomposition, n-octylthiirane

oxide yields to a benign hydrocarbon, the 1-decene, and gaseous sulfur monoxide—no water soluble moieties are formed (Figure 1).

Surfactants are commonly characterized by the critical micelle concentration (CMC), the minimum concentration above which micelles form while dispersed within the bulk phase. The creation of micelles results in changes of the solution physical properties, including stabilization of a dispersed phase and changes in the interfacial properties. These changes in properties enable simple determination of the CMC.

In general, commercially available surfactants exhibit CMCs in the range of 0.5 mM to 20 mM. For instance, the well established surfactant sodium dodecylsulfate (SDS) exhibit a CMC of 8.2 mM. The techniques used to determine the CMC of n-octylthiirane oxide were capillary rise measurements and the dispersion of an aqueous insoluble dye^{14,21}, Sudan III. For each method, multiple aqueous n-octylthiirane oxide solutions of varying concentrations were studied. It is not rare to report CMC values as a range when several techniques are used for measurements; therefore, as shown in Figure 3, the n-octylthiirane oxide's CMC ranges from 6.4 to 8.0 mM. Clearly, n-octylthiirane oxide shows surface-active properties comparable to the surfactants available on the market.

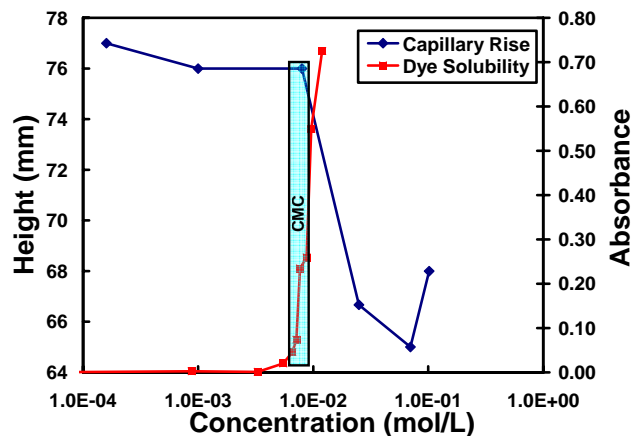
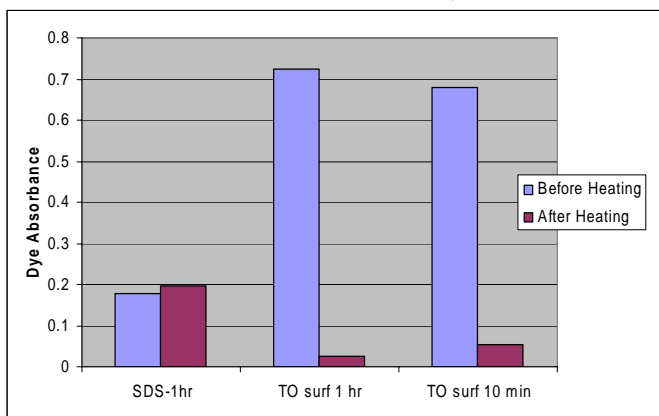


Figure 3 Critical micelle concentration of n-octylthiirane n-octylthiirane oxide in water by capillary rise and dye solubilization.

To test the thermal cleavability, 0.012 M aqueous emulsion of Sudan III dye were heated at 90°C for 10 minutes and an hour, and then cooled to room temperature. The solutions were then sonicated for 30 minutes and allowed to settle for at least two hours prior to filtering.



The UV-vis absorbance was recorded again to determine the dye concentration after decomposition.

Upon decomposition, two products are formed: 1-decene and sulfur monoxide (observed by GC-MS and NMR). Neither possesses surface active character; therefore the emulsion is expected to break. As seen in Figure 4, the large difference in dye concentration before and after heating clearly shows that the micellar structures are not being formed once the surfactant has been decomposed. As expected, the surface-

active properties of sodium dodecyl sulfate (on the far left in Figure 4) remain unaffected after one hour of heating at 90 °C. In contrast, the n-octylthiirane oxide under the same conditions shows an almost complete loss of surfactant activity. Furthermore, after being subjected to 90°C for only 10 minutes, the decomposition has already taken place yielding to a comparable and irreversible loss of activity.

The n-octylthiirane oxide is an efficient surfactant that can be easily cleaved to form 1-decene and sulfur monoxide upon moderate heating (90 °C). Because the two products from the heat-induced decomposition are neither surface active nor water soluble, it represents a major step forward for the cleavable surfactant technologies. n-octylthiirane oxide is an excellent candidate to test the viability of “smart” molecules for surfactant technologies; however, it is a “sacrificial” surfactant due to the instability of SO and it still requires a temperature of around 90 °C to decompose at a reasonable rate – a disadvantage for heat sensitive products.

Piperylene Sulfone Switch

The reversible retro-cheletropic scission of piperylene sulfone. shown in Figure 6, provides a basis for a reversible surfactant. Piperylene sulfone is a liquid at room temperature (mp = ~-12 °C), in contrast to the higher-melting sulfones made from butadiene (mp = 64-65 °C), isoprene (mp = 63-64 °C), and dimethylbutadiene (mp = 134-136 °C).²²

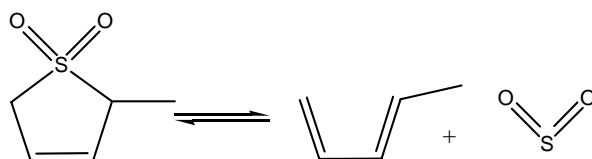


Figure 5. Reversible synthesis of piperylene sulfone from piperylene and SO₂.

Further, piperylene sulfone has a reasonable decomposition rate at moderate temperatures.²³ Figure 10 shows that the piperylene sulfone decomposition occurs both more rapidly and at a lower temperature than other sulfones.

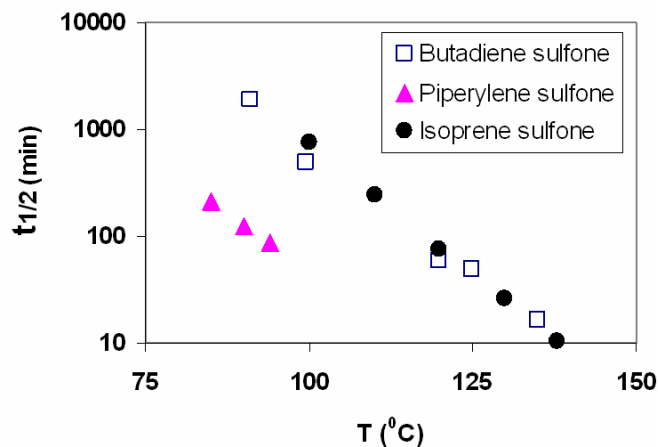


Figure 6. Thermal decomposition of sulfones²³

Upon decomposition, piperylene sulfone releases two products: 1,3-pentadiene and sulfur dioxide via a similar pericyclic mechanism as thiirane oxide. 1,3-pentadiene still polymerizes but much less readily than ethylene. Even more importantly, sulfur dioxide is a stable gas that can be recycled along with the 1,3-pentadiene to re-form the solvent. This reversible process is not only feasible, it is economically and ecologically advantageous.

Contrary to the one-way thiirane oxide surfactant, a sulfolene head-group can yield a truly reversible surfactant. We are investigating 2,5-dihydro-3-thiophenecarboxylic acid-1,1-dioxide octyl ester. Upon decomposition, the sulfolene ring forms one molecule of a butadiene derivative and one molecule of sulfur dioxide (Figure 7). Sulfur dioxide is a stable gas and can be used to

re-form the surfactant providing a two-way switch that is unavailable with the thiirane oxide head-group.

UV light is an attractive trigger to induce decomposition of surfactants, as it is a non-destructive energy source for most chemicals. For a cleavable surfactant to respond to a UV light stimuli, appropriate functionality must be designed into the molecular structure (Figure 8). Therefore, we are synthesizing and investigating 2,5-dihydro-3-thiophenecarboxylic acid-1,1-dioxide octyl ester (Figure 7) and 4-(n-octyl)styrene thiirane oxide (Figure 8) and their properties including:

- Surface-activity
- Decomposition
- Nature of the micelles
- Efficiency as a labile surfactant when applied to reactions.

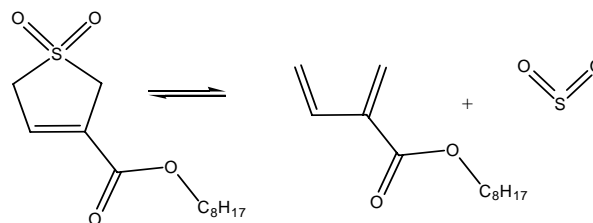


Figure 7 Reversible decomposition of 2,5-dihydro-3-thiophenecarboxylic acid-1,1-dioxide octyl ester

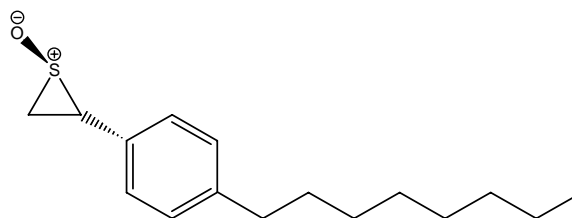


Figure 8. 4-(n-octyl)styrene episulfoxide – photo labile surfactant

Reversible Ionic Liquid Switches

A third potential route to switchable surfactants is based on reversible ionic liquids. As previously mentioned, a “smart” solvent may change from a polar to non-polar, facilitating the separation, which is often difficult with highly polar solvents like DMSO and ionic liquids. Ionic liquids (ILs), salts that are liquid at (or near) room temperature, have gained tremendous attention over the last several years. Besides being “super” solvents, ionic liquids have non-detectable vapor pressure making them even more attractive. Unfortunately, one of their major drawbacks for using ILs as a reaction media lies in the separation. It often requires great efforts to isolate the products from ionic liquid media due to difficulties associated with 1) distillation – negligible vapor pressure; 2) precipitation and crystallization – solid salt formation and 3) liquid extraction – water sensitivity of ILs..

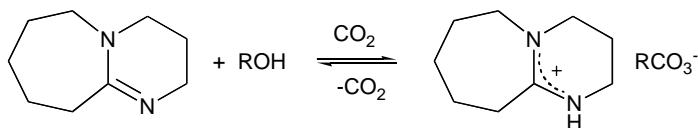


Figure 9. Reaction of DBU, alcohol, and CO₂ to form ionic liquid.

The concept of “switchable” or “smart” ionic liquids is a powerful alternative to ease the separation step and remediate the current drawbacks. In conjunction with Dr. Philip Jessop at Queen’s University in Ontario, Canada, we have developed a solvent that switches from a molecular liquid (non-ionic) into an IL upon simple exposure to CO₂ gas, and then turns back to the molecular liquid upon N₂ or Ar gas bubbling.

Figure 9 above illustrates this conversion where exposing a 1:1 mixture of DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene) and an alcohol to carbon dioxide will *reversibly* form an ionic liquid.

This polar-to-nonpolar switchable ionic liquid was recently reported for the reversible reaction of a 1:1 mixture of DBU and 1-hexanol with CO₂.²⁴ Spectroscopic determination yielded an E_T30 value of 184 kJ / mol for the DBU liquid under N₂ pressure and a value of 222 kJ / mol under CO₂ pressure for the IL. In other words, the polarity of the solvent is switched from nonpolar, comparable to chloroform, to a polar solvent, comparable to dimethylformamide or propanoic acid. Characterization of the DBU ionic liquid by ¹H and ¹³C NMR spectroscopy and conductivity measurements have confirmed the [DBUH]⁺[RCO₃]⁻ salt. We are continuing this work to look at potential reversible surfactant applications.

Potential Impacts

This work will be a significant advance in the design of cleavable surfactants. In addition to the environmental impact from reducing contaminated aqueous wastes, the cleavable surfactant will enhance profitability for the manufacturer by reducing both the quantity and the level of contamination of the aqueous waste stream. The surfactant n-octylthiirane oxide displays the desired properties of a cleavable surfactant. It has a similar CMC to many commercially available surfactants, and it shows complete loss of surface activity by simple stimuli such as heat. As the polar group is completely cleaved in less than ten minutes at 90 °C; both the temperature and the rate are convenient to scaleable chemical processes. Furthermore, conversion to non-surface active agents was demonstrated. We are currently investigating a number of switchable surfactants as well as potential applications.

Applications of switchable surfactants may be found in emulsion polymerization, pharmaceuticals manufacture, or other commercial chemical processes. One potential application is the synthesis and stabilization of metallic nanoparticles within the switchable surfactant media. Over the past 10 years, a great deal of progress has been made with the development of simple techniques for metallic nanoparticle synthesis and stabilization beginning with the work of Brust et al.²⁵ This method uses phase transfer catalysts and thiol stabilizing ligands for the synthesis. More recent developments have investigated metallic nanoparticle synthesis in emulsion systems where the surfactant acts as a phase transfer agent and a nanoparticle stabilizing ligand.²⁶ Using a switchable surfactant as a particle stabilizing agent would enable reversible functionalization of metallic nanoparticles for directed assembly.

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