SAND2006-4566P

Thermally Cleavable Surfactants based on Diels-Alder Chemistry

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Abstract
We have developed, characterized, and patented a class of thermally cleavable surfactants that are based upon the classic Diels-Alder reaction. The thermally-triggered weak-link is located between the hydrophilic and hydrophobic sections of the surfactant, thus enabling the loss of any intrinsic surface-active properties after exposure to mildly elevated temperatures. These surfactants possess physico-chemical properties that are very similar to analogous alkylaryl surfactants, and have been shown to effectively lose all surface active properties after exposure to mildly elevated temperatures for a sufficient period of time.

Introduction
The development of cleavable surfactants has been a growing field in surfactant science in recent years.[1] Cleavable surfactants are typically defined as molecules that undergo a chemical or physical change of the parent molecular structure resulting in a change and/or loss of surface-active behavior. The realization of commercially available cleavable surfactants are thought to have utility in industrial practices where foaming or persistent surface-active properties must be diminished after their initial use, in green chemistry where biodegradability is of primary concern, in the synthesis of materials, and in biomedical drug delivery where surfactants could be removed through biological mechanisms.[1] The incorporation of a cleavable linkage into surfactant molecules could solve this problem by allowing the removal of the surfactant templates through the triggered, on-demand formation of small, easily removed fragments.

There are several examples of cleavable surfactants that have been previously reported based on functional groups that are susceptible to alkaline or acid hydrolysis. These surfactants operate within defined pH ranges and are removed from the system by adding an appropriate amount of acid or base. Examples of acid-labile surfactants include cationic surfactants with cyclic acetals such as cationic surfactants derived from ortho esters,[2] alkylglucosides,[3] bromopropionaldehyde,[4] and both cyclic[5] and noncyclic ketals.[6] Alkaline-labile surfactants include surfactants that contain cleavable ester moieties such as choline esters,[7] esters of quaternized amidoamines[8] and ethanolamines,[9] as well as esters derived from naturally occurring sugars (i.e. glucose, sucrose, and sorbitol) combined with fatty acids.[10] One disadvantage of these hydrolysable surfactants is the requisite addition of acid or base to degrade the surfactant, which may prove to be an economically disadvantageous process or damaging to the environment. Other labile

elements that have been incorporated into surfactants include UV sensitive components, such as alkylarylketone sulfonates[11] and diazosulfonates[12] that degrade upon irradiation.

Our Approach

We have synthesized, characterized, and patented a new class of cleavable surfactants[13] that incorporate a thermally cleavable Diels-Alder adduct as the chemical weak link within the surfactant molecular structure.[14] The classic Diels-Alder reaction involves a [4 + 2] cycloaddition reaction between a diene and a dienophile.[15] We utilized this reversible Diels-Alder (DA) reaction between functionalized furans and maleimides as the basis for our thermally cleavable surfactants (Figure 1).[16] This methodology has been previously utilized for the integration of furan-maleimide DA adducts into molecules to produce thermally responsive foams,[17] encapsulants,[18] adhesives,[19] as well as dendrons and dendrimers that can reversibly self-assemble.[20] The process of adduct formation typically occurs at moderate temperatures (25 - 60 ^{o}C), whereas dissociation occurs at slightly elevated temperatures (> 60 ^{o}C), as shown in Figure 1. The temperatures required for cleaving of these DA surfactants are significantly lower than those currently utilized in the removal of traditional surfactants through calcination, which are typically on the order of 450-500 ^{o}C. Surfactant molecules that contain cleavable furan-maleimide DA adducts are, therefore, attractive candidates for use as surface-active materials for processes that require surfactant removal using a non-invasive and relatively mild thermal trigger. We have synthesized two of these surfactants with differing headgroup moieties – carboxyolate and phenolate, but are identical in the nature of their alkane tails. These surfactant headgroups can be deprotonated using an excess amount of an appropriate base, such as potassium hydroxide, to form freely water soluble surfactants (Figure 2).

Diels-Alder Surfactant Properties

Determining the extent to which it these materials are surface-active agents, we needed to confirm the presence of micellar aggregates, as well as determine the critical micelle concentration (cmc) above which these aggregates form. The solubilization of a water-insoluble dye is an effective method that indicates the presence of micelles and has been used since the 1960s. UV-Vis measurements were conducted to monitor the absorbance of each dye as a function of surfactant concentration in the aqueous samples. After a certain concentration is reached for each surfactant system, the values for each dye at their absorbance wavelength maximums are observed to increase monotonically with increasing surfactant concentration. This increase in dye absorbance above a specific surfactant concentration indicates the presence of micelles, and is attributed to increased dye solubilization as the number of micelles increases. The cmc values measured using this technique are 0.6 mM and 2.7 mM for the phenolate and carboxylate surfactants, respectively.

We have also utilized surface tensiometry to determine the degree to which these surfactants impact the properties of the solutions they form. Figure 3 presents the responses of dynamic surface tension (operated in equilibrium mode) as a function of concentration for the carboxylate surfactant. This surfactant exhibits the classical

dependence of surface tension as a function of concentration, with a constant high surface tension region at low concentrations followed by a decreasing linear region over a concentration range, followed again by a relatively constant region at higher concentrations. In a comparison between the phenolate and carboxylate surfactants in a recently published report, we found that the phenolate-based anionic surfactant assembles at the liquid-gas (L/G) interface with tighter packing.[14] The cmc's calculated from the surface tension data of the carboxylate and phenolate are 9.3 mM and 2.5 mM, respectively.[14] Overall, the cmc's determined through this method are higher than those obtained by the measurement of dye solubilization described above. This discrepancy is generally attributed to static (dye solubilization) vs. dynamic (surface tension) measurements of the microenvironment.[21] From the perspective of surface tension values at concentrations greater than the cmc, the phenolate attains a lower surface tension and thus appears to be a more active surfactant at the L/G interface than the carboxylate.

When exposed to elevated temperatures (95 ^{o}C) the solutions are observed to undergo a marked color change to a dark yellow liquid with increased turbidity (Figure 4). Samples were also observed to phase separate when allowed to stand overnight after exposure to this temperature. The response of the surface tension for 20 mM solutions of the phenolate and carboxylate were recorded as a function of time exposed to 95 ^{o}C, and the data for the carboxylate is presented in Figure 3. Both surfactants are observed to undergo an irreversible loss of surface tension after exposure to this temperature, indicating that the DA fragmentation has occurred. The surface tension value for the carboxylate reaches the value of water at 25 ^{o}C (~72.1 mN/m) in approximately 1 h and then stabilizes, whereas it was observed that the phenolate requires 1.5 h to reach the same plateau range.[14] This difference is attributed to the different cmc's of the carboxylate and phenolate surfactant, as a lower concentration for the phenolate surfactant must be reached before observing a substantial loss of surface tension when compared to the carboxylate DA surfactant**,** which has a higher cmc. It should also be noted that the measurements of surface tension were taken after the samples had been cooled to ambient conditions, and are convincing evidence that the dissociation accompanying the retro DA is irreversible in micelles.

Summary

We have developed a novel class of thermally degradable cleavable surfactants. Commercially available cleavable surfactants would enable industrial practices where it is desirable to diminish foaming or surface-active properties over time, in drug delivery, and as removable templates. They could prove useful in such diverse fields as textile processing, electronics fabrication, sample management, wastewater processing, cleavable phase transfer reagents, and as removable templates for the construction of microporous zeolitic materials as well as templates of complex hierarchical materials. Stable in aqueous solutions, these thermally cleavable Diels-Alder surfactants possess good wetting characteristics. When exposed to elevated temperatures (more than 50 ^{o}C), they irreversibly degrade in water, yielding hydrophilic and hydrophobic fragments. These surfactants may prove useful in surface-active applications in which a noninvasive thermal trigger would be an attractive way to deactivate or remove the surfactant, and/or modify the surface-active properties of the solutions.

Note
This work was supported by the United States Department of Energy (US DOE) under contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE.

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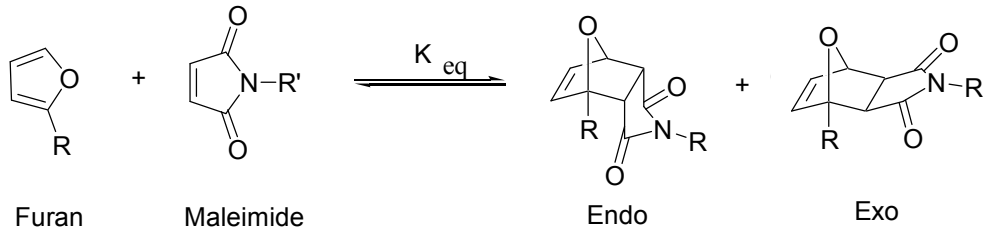

Figure 1. Furan-maleimide Diels-Alder adduct formation and dissociation (reproduced from Ref. 14 with permission of the American Chemical Society).

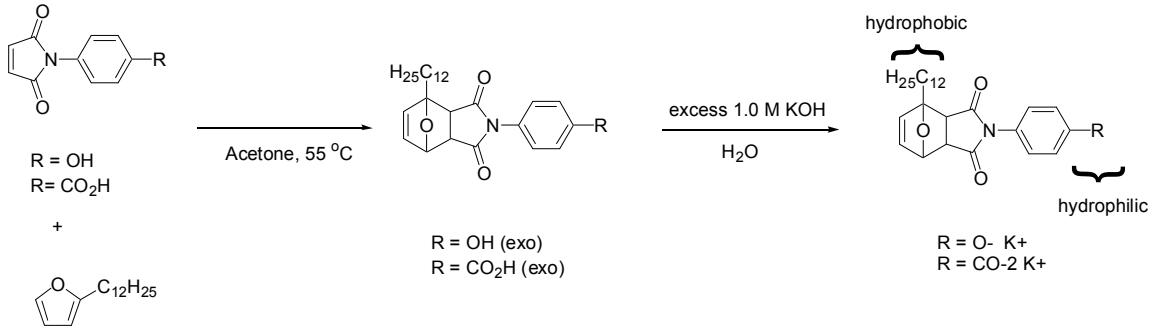

Figure 2. Synthesis route to surfactants with Diels-Alder adducts located between hydrophilic and hydrophobic segments that possess two different headgroup moieties (reproduced from Ref. 14 with permission of the American Chemical Society).

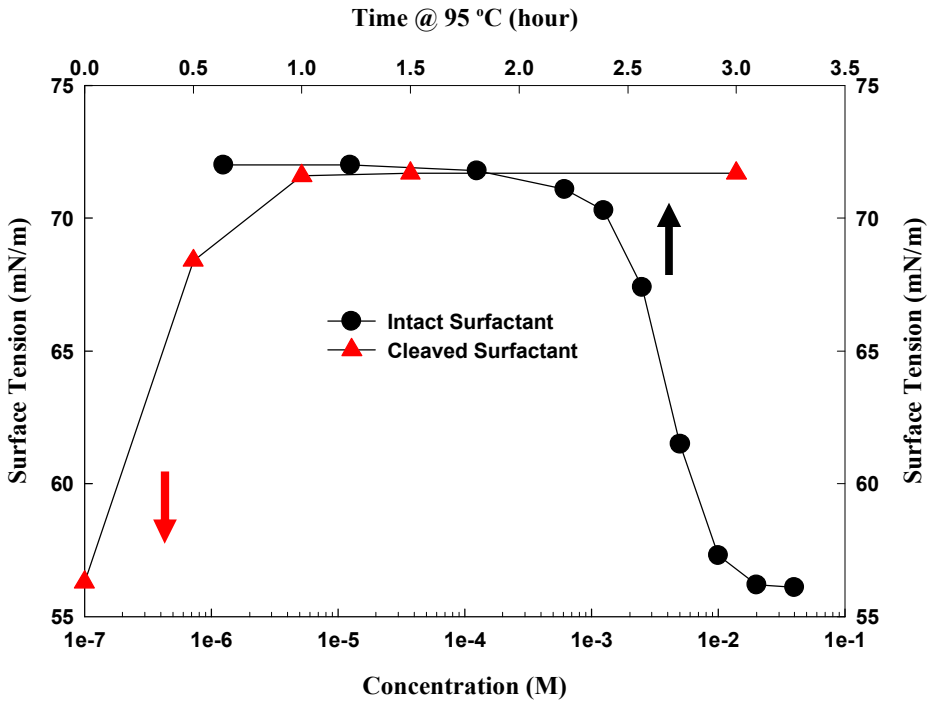

Figure 3. Graph showing the typical surface tension properties of carboxylate Diels-Alder surfactants as a function of concentration (black) and during the cleaving process as a function of time (red) of a 20 mM solution of the carboxylate surfactant (reproduced from Ref. 14 with permission of the American Chemical Society).

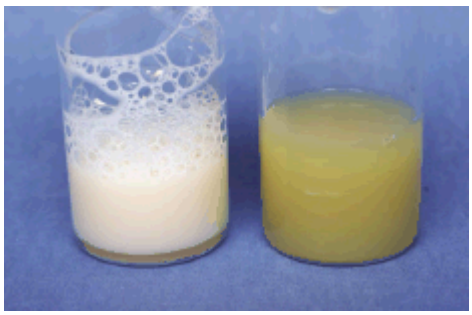

Figure 4. Digital image of a dye-containing emulsion with 20 mM of the carboxylate Diels-Alder DA surfactant before and after exposure to 95 ^{o}C for 2h.

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