Next Generation Carbohydrate-Based Surfactants

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Introduction
Carbohydrate-based surfactants represent an increasingly important class of nonionic surfactants that include products such as alkyl polyglycosides (APGs), sorbitan esters (trade names SPAN® and Tween®), and methyl glucoside esters (MGEs). In addition to being renewable, carbohydrate-based surfactants have a number of favorable attributes including desirable detergency properties and low toxicity. However, carbohydrate-based surfactants generally incorporate either base-labile ester linkages (SPAN®, Tween® and MGEs), or acid-labile C-glycosyl linkages (APGs) into their structures. The instability of these functionalities limits the use of carbohydrate-based surfactants in certain applications and thus limits their broader adoption. One potential way to address this issue is to replace these traditional linkages with a more stable C-glycoside linkage (Figure 1).

The C-glycoside Surfactant Technology
Research at P2 Science is focused on commercializing a new class of carbohydrate-based surfactants developed through a fundamental design approach that integrates efficacy, cost, and environmental and human health criteria across the lifecycle, from extraction to disposal. The surfactants of interest, described generally as C-glycosides, fall into two series – linear and cyclic – the general structures of which are shown in Figure 2. These molecules are prepared using a novel synthetic route that adheres closely to the principles of green chemistry, such as atom economy, step economy, and reliance on renewable feedstocks.

Figure 2. Representative compounds from the two proposed C-glycoside surfactant series.

The synthesis of these surfactants proceeds through a nonulose intermediate that can be used as a scaffold for the construction of either linear or cyclic enone-containing C-glycosides. Accessing through an enamine-catalyzed aldol condensation, the C-glycoside surfactants are obtained in very good yield under mild conditions in a single step without the need for extensive purification. The C-glycoside surfactants possess a number of desirable performance properties including dramatic surface tension reduction and tunable foaming properties (Table 1 & Figures 3 & 4).

Table 1. Surfactant properties for several representative carbohydrate based surfactants.

As can be seen in Figure 3 and Table 1, the C-glycosides behave similarly to their O-glycoside counterparts in terms of CMC and interfacial tension reduction. Further, it appears that the CMC is directly related to the hydrophobic-lipophilic balance (HLB), as calculated according to Griffin’s Method. The HLB increased, which is a common phenomenon often attributed to polydispersity of micelles. As compared to SDS, the foaming properties of the C-glycosides were modest, with Cyclic 2 exhibiting virtually no excess foam after 5 min (Figure 4). However, when combined with SDS as a 20% solution, the foaming properties exceeded that of SDS alone and the foam height remained unchanged over 3 min, suggesting that the C-glycosides have a foam enhancing and stabilizing effect in the presence of an anionic surfactant.

Conclusions
Presented here is a structurally distinct class of C-glycoside surfactants that can be easily synthesized and characterized. The C-glycosides presented fall into two series – linear and cyclic – and can be made from a variety of carbohydrate feedstocks, including glucose, lactose, xylose, and galactose. Synthesis requires minimal energy inputs and uses only mild reagents. The C-glycosides obtained are highly effective at reducing surface tension, can solubilize organic materials as effective as, if not better than other carbohydrate-based nonionics, and have tunable properties. Two representative cyclic C-glycosides were evaluated for acute toxicity with regard to Pimephales promelas and Daphnia magna. They were found to have toxicity values that closely mirrored those of APGs, which are generally regarded as safe (GRAS) according to the U.S. Food and Drug Administration. Further, these surfactants were designed to be inherently pH stable and can thus be considered for use in a broader range of applications than traditional carbohydrate-based surfactants.

Future work will include the continued characterization of the the C-glycoside surfactants and their derivatives, and will include full evaluation of these compounds for safety and environmental performance. Additionally, algal lipids will be evaluated as feedstocks for the hydrophobic portion of the surfactant molecules.

Figure 3. CMC curves for representative C-glycoside surfactants.

Figure 4. Ross-Miles Foam Test for representative C-glycosides, alone and with SDS.