



Massachusetts Toxics Use Reduction Institute

University of Massachusetts Lowell

Polysaccharide Based Surfactants as Alternative to Nonylphenol Ethoxylates in Laundry Detergents

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Polysaccharide Based Surfactants as Alternative to NonylphenolEthoxylates in Laundry Detergents

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1 Background

The largest markets for surfactants are primarily, household detergents, industrial cleaners and personal care products (as shown in **Figure 1**). With the remarkable ability to influence the properties of surfaces and interfaces, surfactants are essential ingredients in thousands of products.

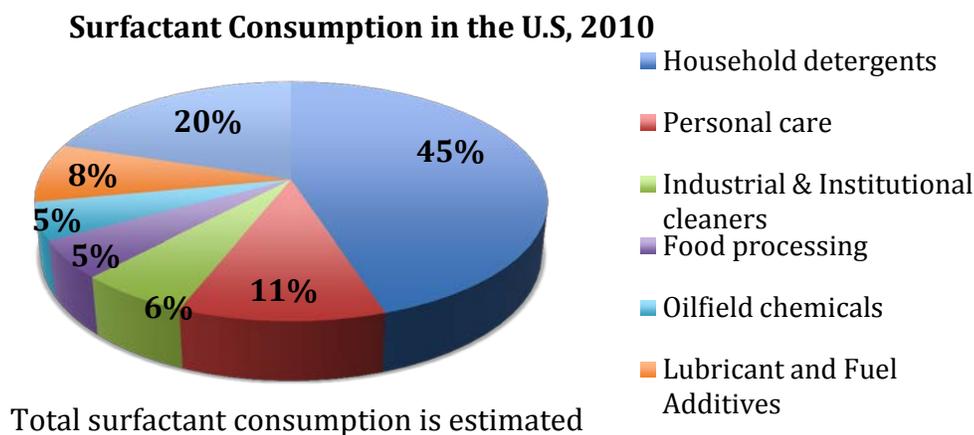


Figure 1 Surfactant consumptions according to market segment¹

Recently, there has been tremendous interest in the manufacture and use of non-toxic/'greener' surfactants, particularly for the household cleaning sector. Although the surfactant industry uses the term 'natural surfactant' to indicate the presence of bio-based ingredients in their product lines, the industry as a whole still heavily relies on petrochemical feed stocks and harsh chemical synthesis for the manufacturing of surfactants. The manufacturing processes rarely comply with principles of green chemistry². In addition, after use, most commercially available surfactants are either non-biodegradable or degrade to produce more toxic products as in the case of Nonylphenol ethoxylates (NPEs)^{3,4}. Therefore the surfactant industry as a whole is exploring 'greener' surfactants suitable for large variety of applications.

2 Research goals and objectives

During 2010-2011 as part of TURI-funded project, we had demonstrated the possibility of modifying naturally occurring polysaccharides like polygalacturonic acid (PGA) to yield a new class of bio-based surfactants. The goal of the project was to create a new class of effective surfactants as a replacement to non-ionic surfactants such as nonylphenol ethoxylates.

The goals for the second phase of this project (2011-2012) were to:

- (1) Explore other low cost polysaccharides-based starting materials for the synthesis of the surfactants and further characterize the surfactant products.
- (2) Scale-up the reaction and carry out a variety of tests to ensure that the polysaccharide based surfactants were suitable for being formulated into cleaning products such as laundry detergents.
- (3) Explore the possible use of these new bio-based surfactants in cleaning formulations, specifically in laundry detergents.

These goals were met by pursuing the following objectives:

- (1) Naturally occurring polysaccharides, alginic acid, obtained from brown sea algae was selected as a starting material in addition to PGA and taurine.
- (2) Surfactants synthesized were characterized using FTIR spectroscopy and surface tensiometry. The effect of temperature on surface tension and wettability of these surfactants were also studied.
- (3) Variety of tests such as pH stability, foam stability, cloud point, cleaning efficiency of dirt and soil re-deposition studies were carried out for these surfactants.
- (4) Surfactants were compounded into actual detergent formulations as a 'drop in' replacement for NPEs in collaboration with a Massachusetts based company - Alpha Chemical Services, Inc. Stoughton, MA. The cleaning efficiency of these laundry detergent formulations were also evaluated.

3 Materials and Methods

3.1 Materials

- a) **Polygalacturonic Acid (PGA):** PGA also known, as pectin acids are water insoluble, transparent gelatinous acid, existing in ripe fruits and vegetables. It is a product of pectin degradation, which can be found in cell wall. PGA derived from pectin was particularly of interest due to its wide availability, low cost, and obtained from fruit wastes (i.e. fruit peels) generated from the juice industry⁵. The idea of utilization and conversion of a waste product to a commodity chemical (i.e. surfactant) to replace commercially available surfactants is very encouraging.
- b) **Alginic Acid (ALG):** Low cost and more readily available algae-based polysaccharide was also explored as possible starting material. Algae represent an interesting source of biomass. It is an efficient autotroph, in terms of yield per acre of polysaccharides, versus others such as fruits, corn or sugar. It does not have a competing food application. Non-food based feedstock are always more favorable starting materials from a sustainability standpoint.
- c) **Taurine:** 2-aminoethanesulfonic acid (Taurine) [$>99\%$] a naturally occurring amine was purchased from Sigma Aldrich (St. Louis, MO) and used as received for hydrophilic modification of water insoluble polysaccharide.

3.2 Method of synthesis (General procedure for hydrophilic modification of polysaccharides)

a) Conventional Synthesis

PGA and ALG are water insoluble due to its high molecular weight and intermolecular chain hydrogen bonding. The amidation of PGA or ALG using naturally occurring amine such as taurine (2 aminoethanesulfonic acid) is a novel

approach to the hydrophilic modification of these polysaccharides. The presence of the sulfonic acid groups in the polymer structure will render the modified polysaccharides greater hydrophilicity in various pH conditions. The amidation of PGA or ALG were performed by coupling of the carboxyl groups with an amine containing entity (i.e. taurine), in the presence of a coupling agent to yield sulfonated-PGA (PGA-SO₃) and sulfonated-ALG (ALG-SO₃).

This reaction was carried out at room temperature in aqueous medium, providing a one-pot “green” synthesis method, therefore minimizing the use of harsh organic solvents. This work establishes a general methodology for hydrophilic modification of any polysaccharide, thereby opening new possibilities for the synthesis of novel amphiphilic, non-toxic and biodegradable surfactants.

b) Microwave Synthesis

PGA and taurine are polar molecules that can absorb microwave irradiation. Therefore the microwave-assisted synthesis of PGA-SO₃ was also explored. Microwave reactors can deliver heat more efficiently and eliminate the need for coupling agent that is otherwise required for the synthesis of polysaccharide-based surfactants. Microwave reactions were performed using a Biotage Initiator™ system with heating specifications shown in **Table 1**.

Table 1 Biotage Initiator™ Microwave Heating Specification

Temperature	40-250 °C (104-482 °F)
Pressure range	0-20 bar (2 MPa, 290 PSI)
Power range	0-400 W at 2.45 GHz –power controlled automatically to achieve desired temperature
Reaction vials	4 sizes: 0.2-0.5, 0.5-2, 2-5, 10-20 mL
Vial volume range	0.5-15 mL
Agitation	Variable magnetic stirrer (300-900RPM)

4 Characterization of modified polysaccharide surfactants

4.1 Functionalization Characterization

Fourier Transform Infrared (FTIR) spectroscopy was used to qualitatively assess functionalization and confirm amidation. Meanwhile, the degree of functionalization was also quantitatively assessed using elemental analysis technique performed by Galbriath laboratories, Knoxville, TN.

4.2 Surface activity measurements using Du-Nouy Ring Tensiometry

Surface tension of polysaccharide-based surfactants (PGA-SO₃ and ALG-SO₃) was measured and compared to unmodified PGA, ALG and commercial surfactants, Triton X-100 and Sodium Lauryl Sulfate (SLS). After modification, surface tension of PGA significantly dropped from 61.64 mN/m to 33.52 mN/m for PGA-SO₃ and 64.3 mN/m to 38.6 mN/m for ALG-SO₃. These values are comparable to both commercial surfactants, Triton X-100 (31.87 mN/m) and SLS (33.49 mN/m). ALG-based surfactant, ALG-SO₃ and its unmodified form exhibit higher surface tension than PGA-based surfactant due to its higher viscosity owing to its higher molecular weight.

4.2.1 Effect of Temperature on Surface Tension

Studying the effect of temperature on surface tension is important for determining suitability in cleaning applications under different conditions. Dishwashing and hot-water laundry detergents use higher temperature. For cold-water laundry detergent applications the temperature requirements are obviously different. It was observed that at higher temperatures, surface-activity is marginally higher (low surface tension) and at lower temperatures, surface-activity dropped (increase in surface tension). These results suggest that the polysaccharide-based surfactants will work better at higher temperatures.

4.3 Evaluation of Wettability/Contact Angle measurement

Wettability refers to the ability of a surfactant solution to spread over a given surface⁶. Surfactants accomplish this by lowering the energy barrier between the solvent and the substrate. Wetting can be determined by measuring the contact angle of a drop of surfactant solution sitting on the substrate of interest. Contact angle is the angle between the substrate surface and the droplet. The closer the contact angle is to zero, the better the wetting agent (surfactant).

Results obtained show that PGA-SO₃ can wet glass substrate much better than unmodified PGA. By reducing the surface tension of a liquid, wettability is improved since contact angle and surface tension are related by Young's Equation ($\gamma_{SL} + \gamma_{LV} \cos\theta_c = \gamma_{SV}$). PGA-SO₃ has comparable contact angle to Triton X-100 and SLS on glass substrate as well as on hydrophilic type dirt. However, PGA-SO₃ exhibits poor wettability on hydrophobic type dirt, (higher contact angle).

4.4 Evaluation of Acid/Base Stability

Many sugar-derived surfactants undergo hydrolysis when exposed to acids or bases because the ester link between the hydrophilic and hydrophobic ends is vulnerable, leading to primary degradation⁷. Polysaccharide-based surfactants containing amide linkages are chemically stable and are not easily degraded in acid/alkaline media⁸. Chemical stability could help in heavy-duty household and industrial cleaning formulations. Surfactants were left in acid (pH 3-4) and base condition (pH 9-10) for 30 days and their surface tension were re-measured. The stability of the surfactants in acid and base conditions shows comparable stability to that of commercial surfactants, Triton X-100 and SLS in both acid and base conditions. There is no significant change in surface activity of the PGA-SO₃ even with long exposure to acid/base conditions, which indicates that no significant degradation has occurred.

4.5 Determination of Cloud Point (ASTM D2024)

Cloud Point (C_P) is the temperature at which dissolved components (solids or liquids) are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance (turbid)⁶. Cloud point testing was carried out in accordance to ASTM D2024-09 Standard Test Method for Cloud Point of Nonionic Surfactants⁹. Knowing the cloud point is important for determining storage stability. Storing formulations at temperatures significantly different from the cloud point may result in phase separation and instability. Wetting, cleaning and foaming characteristics can be different above and below the cloud point.

At low temperatures, both Triton X-100 and PGA-based surfactant does not exhibit a cloud point in which no significant change was observed. However, SLS exhibits a cloud point at lower temperature in which it becomes insoluble (Reported $C_P= 4^\circ\text{C}$). Meanwhile at high temperatures Triton X-100 exhibits a cloud point at higher temperature (Reported $C_P 60^\circ\text{C}$) and both SLS and PGA-based surfactant did not exhibit a cloud point at higher temperature. Instead PGA-SO₃ became more clearer (soluble) at higher temperature.

Factors that affect cloud point include (1) Structure and concentration of the surfactant (2) Molecular weight of the surfactant and (3) Presence of additives (e.g. electrolytes, non-electrolytes, organic substances as well as ionic surfactants)⁶. Therefore the high molecular weight of the starting material contributed to the turbidity of the polysaccharide-based surfactant across the board.

4.6 Evaluation of Foam Stability (ASTM D4009)

Foaming is important from an aesthetic point and is a very important consideration in suitability of the detergent in machine-washing applications. Foaming during cleaning helps prevent re-deposition of dirt/soil onto the clean surface¹⁰. However, too much foaming in applications such as dishwashing and laundry detergents causes problems in rinsing off residual foam and clogging of drain lines. This has led the surfactant manufacturers to develop low foaming products. The initial foam volume and the subsequent foam decay were monitored during 45 minutes. Initial

foam height and stability of tests of surfactants show that PGA-based surfactants exhibit poor foaming properties (both foam volume and stability) in comparison to Triton X-100 and SLS.

4.7 Evaluation of Dirt/Soil-Re-deposition (ASTM D4008)

Once the dirt/soil has been detached from the substrate, it is solubilized inside the micelles, emulsified, or in the case of solid particles, dispersed as a suspension in the washing liquid. The emulsions and dispersions of solids are not stable, and often the soil (dirt) re-deposits on the cleaned items. When soil is removed from surfaces, it is important that it should not be allowed to re-adsorb onto the clean surface.

Contaminant and stain removal efficiency of dirt on cotton fabric was tested in accordance to ASTM D4265 – 98 ‘Standard Guide for Evaluating Stain Removal Performance in Home Laundering’ and ASTM D4008 – 95 ‘Standard Test Method for Measuring Anti-Soil Deposition Properties of Laundry Detergents’ to measure the cleaning ability of the surfactants on fabric^{11,12}. Results obtained show that SLS and PGA-SO₃ have good contaminant removal efficiency compared to non-ionic type surfactant, Triton X-100 in deionized water. However in hard water (150 ppm), the contaminant removal of anionic type surfactant is less efficient than non-ionic surfactants.

Anionic types surfactants having negatively charged head groups that are particularly good at keeping dirt away from cotton fabrics preventing soil re-deposition. However anionic type surfactants can be affected by cations (i.e. Ca²⁺ and Mg²⁺), in hard water, which can lead to partial deactivation of anionic surfactants. As the hardness of the water increases (i.e. at higher concentration of calcium and magnesium molecules in the water), the deactivation of the anionic surfactant system also increases. This is the reason for the lower cleaning efficacy of anionic surfactants in hard water.

Unlike anionic surfactants, non-ionic surfactants do not have appreciable charge on the head group, which makes them resistant to water hardness deactivation.

Therefore most laundry detergents are usually formulated to contain both non-ionic and anionic to complement each other's cleaning action.

4.8 Efficacy of Polysaccharide-based Surfactant as a 'Drop in' replacement for NPE in cleaning formulations

PGA-based surfactant was added as a 'drop in' replacement for NPEs in a laundry detergent formulation (Alpha Chemicals Product Name: Towel Laundry, Product Code: 5880) provided by Alpha Chemical Services, Inc. Stoughton, MA. Results obtained show that PGA-based surfactants have comparable cleaning efficiency as commercial surfactants Triton X-100, SLS and Alkyl Polyglycosides (APGs).

5 Conclusion

Polysaccharide-based surfactant derived from polygalacturonic acid (PGA) and alginic acid (ALG) were successfully synthesized and characterized. The polysaccharides were hydrophilically modified with bio-derived taurine to yield amphiphilic polymeric surfactants. FTIR spectroscopy was used to confirm the amidation reactions. Both conventional chemical synthesis and microwave-assisted methods were explored for the synthesis of PGA-SO₃ and ALG-SO₃. The microwave-catalyzed synthesis could be done without the use of a coupling agent at 90°C with a shorter reaction time of 15 minutes as compared to 16 hours by chemical synthesis involving conventional heating.

Water solubility and surface-active properties of PGA were significantly improved after modification. The surface tension of PGA-SO₃ was comparable to commercial surfactants, Triton- X-100 and SLS. PGA-SO₃ showed particularly good cleaning efficiency towards hydrophilic type dirt (i.e. bathroom soil and scum). However due to lack of lipophilic groups, PGA-SO₃ showed poorer cleaning efficiency towards hydrophobic type dirt. Wettability studies of PGA-based surfactant correlated with the trends observed in cleaning efficiency. PGA-SO₃ wets hydrophilic surfaces better than hydrophobic surfaces and hence the cleaning efficiency is much better for hydrophilic type dirt.

PGA-SO₃ and ALG-SO₃ showed good fabric detergency in deionized water compared to non-ionic type surfactant, Triton X-100. However in hard water (with 150 ppm dissolved salts), the contaminant removal of SLS and PGA-SO₃ were less efficient than Triton X-100. Foaming properties of PGA-SO₃ was poor compared to Triton X-100 and SLS. However, PGA-SO₃ is stable in acid and base conditions with no substantial changes in surface tension.

In the drop in replacement tests with Alpha chemical formulation, PGA-SO₃ showed higher surface tension. However its performance in fabric detergency test was comparable to that of triton X-100, which was one of the main goals of the research work. Thus the polysaccharide-based surfactants developed during the course of the project shows great potential for being a drop in replacement to NPE's in the existing laundry detergents. This renders the research attractive from a commercial standpoint as we have already demonstrated that comparable cleaning efficiency can be obtained.

This study establishes a general methodology for hydrophilic modification of polysaccharides, opening new possibilities of creating new classes of novel amphiphilic, non-toxic and bio-derived surfactants.

6 Recommendations

1. The polysaccharide-based surfactants synthesized over the course of this project are not very efficient for cleaning hydrophobic type dirt. The high molecular weight and extensive hydrogen bonding in the polysaccharides limit the solubility and extent of functionalization. Additional hydrophobic modification of the PGA-SO₃ was not possible due to the limited solubility. It is important to develop methods to tune the hydrophilic-lipophilic balance (HLB) such that a range of modified polysaccharide-based surfactants with varying levels of hydrophilic and lipophilic character can be obtained. This can be accomplished by the following:
 - a. Increase extent of functionalization: The extent of hydrophilic functionalization should be increased substantially by changing the solvent system, the catalyst and

reactant ratios. This would also improve water solubility of these polysaccharide-based surfactants.

- b. Lowering molecular weight of PGA and ALG: The possibility of lowering molecular weight of the polysaccharide as a means to improving solubility can also be explored. Lowering molecular weight of polysaccharides can be achieved through depolymerization to oligosaccharides through techniques such as acid¹³ or, enzyme^{14,15,16} catalyzed hydrolysis and by the use of ion exchange resin.^{17,18}
 - c. Hydrophobic modification of water-soluble sulfonated polysaccharides: Further functionalization of hydrophilically modified, water-soluble polysaccharides using long chain fatty acids can be achieved. Where possible the functional groups required for hydrophobic modification will also be sourced from natural products to maintain the composition of the surfactant to be 100% bio-based. For example, natural oils can be used for hydrophobic modification.
2. Characterization: In addition complete structural characterization of the modified polysaccharide using techniques such as NMR spectroscopy should also be attempted. Also determining the molecular weight is important to confirm no chain scission or hydrolysis occurred during the modification process.
 3. Dermal toxicity and biodegradability studies: Acute dermal irritation and toxicity studies are required before actual use in cleaning formulations. ASTM F719 - 81(2007) 'Standard Practice for Testing Biomaterials in Rabbits for Primary Skin Irritation' should be carried out to provide fundamental data to manufacturers. Studying PGA-SO₃ end-of-life in terms of biodegradability is also important to determine if these surfactants are able to biodegrade safely in the environment without producing toxic by-products.

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