Abstract: Sulfation or sulfonation of biopolymers such as starch, chitosan, dextrins, gums and the like is conducted in an ionic liquid such as a quaternary ammonium salt. Detergent compositions containing the sulfated or sulfonated reaction product are suitable for fabric cleansing.
METHODS FOR MODIFYING BIOPOLYMERS IN IONIC LIQUIDS

FIELD OF THE INVENTION

The present invention relates to methods for modifying or derivatizing biopolymers in an ionic liquid medium to provide modified biopolymers. The preferred method comprises at least partially dissolving a biopolymer in an ionic liquid and adding to the mixture a modifying agent having a functional moiety such that the resulting modified biopolymer contains the functional moiety. Specifically, the method involves modifying the biopolymer with sulfate or sulfonate moieties. The invention is further relates to surface care, fabric care and air care compositions containing such modified polymers.

BACKGROUND OF THE INVENTION

Various synthetic polymers are typically produced from petro-chemical sources via well-known chemical processes. In recent years, the industry has renewed its focus on biopolymers from environmentally friendly, renewable sources of plants, animals and other living organisms. Extracting or separating the biopolymers from their natural sources often employs large quantities of volatile organic solvents or other undesirable chemical solvents. It is a desirable next step to employ a "green solvent" to extract and process biopolymers.

In recent years, ionic liquids have been extensively evaluated as environmental-friendly or "green" alternatives to conventional organic solvents. Ionic liquids have been used to dissolve or treat cellulosic materials and starch. Such applications are described in US 1,943,176; US 6,824,599; WO 05/17001; WO 05/17252; and WO 05/23873.

Generally speaking, ionic liquids refer to a specific class of salts which are liquids at temperatures of 100°C or below. Ionic liquids have very low vapor pressure and generate virtually no hazardous vapors. Moreover, ionic liquids are composed of charged species, which provide a highly polar medium useful in various applications, such as extraction, separation, catalysis and chemical synthesis media.

Additionally, ionic liquids have been shown to be effective in applications where water-based chemistry can be problematic (for example, applications involving proton transfer or nucleophilicity), or in applications where certain coordination chemistry could have a damaging effect on the substrates involved.
Therefore, it is desirable to take advantage of the highly polar and environmentally friendly nature of the ionic liquids in modifying and/or derivatizing biopolymers to provide modified biopolymers.

It is also desirable to provide modified biopolymers useful in various applications via green chemistry employing environmentally friendly starting materials and processes.

SUMMARY OF THE INVENTION

In broad terms, the invention is directed to methods for preparing a modified biopolymer in an ionic liquid. In one aspect, the method comprises reacting a sulfation or sulfonation agent, or mixtures thereof, with a saccharide-based biopolymer (hereinafter "biopolymer") in a reaction medium comprising an ionic liquid. A preferred, but non-limiting, embodiment comprises at least partially dissolving said biopolymer in an ionic liquid and adding a sulfation or sulfonation agent thereto, such that the biopolymer is converted to a modified biopolymer containing a sulfate or sulfonate functional moiety. Specifically, the present invention is directed to sulfation or sulfonation of biopolymer saccharides, such as starch, chitin, chitosan, dextran, maltodextran, dextrin, maltodextrin, gums, agar, alginates, and the like.

In further embodiments, the invention is directed to fabric care, surface care and air care compositions containing a sulfated or sulfonated biopolymer formed according to the methods disclosed herein.

Additional embodiments, objects and advantages will be more fully apparent in view of the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for modifying and/or derivatizing the biopolymers in an ionic liquid medium with functional groups such as sulfate, sulfonate, and mixtures thereof.

Suitable biopolymers are at least partially soluble in an ionic liquid. The biopolymers may be obtained from saccharides, which may be harvested from bacteria, fungi or plants. Suitable saccharides include, but are not limited to, starch, chitin, chitosan, dextran, maltodextran, dextrin, maltodextrin, gums, agar, alginates, and the like.
The sulfated or sulfonated biopolymers may be used in various applications, including but not limited to, fabric care compositions, surface care compositions and air care compositions.

IONIC LIQUIDS

The term "ionic liquid" as used herein refers to a salt that has a melting temperature of about 100°C or less, alternatively of about 60°C or less, or in a further alternative, of about 40°C or less. Some ionic liquids exhibit no discernible melting point (based on DSC analysis) but are "flowable" at a temperature of about 100°C or below; other ionic liquids are "flowable" at a temperature of from about 20 to about 80°C. As used herein, the term "flowable" means that the ionic liquid exhibits a viscosity of less than about 10,000 mPa-s at temperatures of about 100°C or below or from about 20 to about 80°C. Thus, the "fluid state" of an ionic liquid is meant to encompass all of these embodiments, including the molten state and the flowable state.

It should be understood that the terms "ionic liquid", "ionic compound", and "IL" refer to ionic liquids, ionic liquid composites, and mixtures (or cocktails) of ionic liquids. The ionic liquid can comprise an anionic IL component and a cationic IL component. When the ionic liquid is in its liquid form, these components may freely associate with one another (i.e., in a scramble). As used herein, the term "cocktail of ionic liquids" refers to a mixture of two or more, preferably at least three, different and charged IL components, wherein at least one IL component is cationic and at least one IL component is anionic. Thus, the pairing of these three cationic and anionic IL components in a cocktail would result in at least two different ionic liquids. The cocktails of ionic liquids may be prepared either by mixing individual ionic liquids having different IL components, or by preparing them via combinatorial chemistry. Such combinations and their preparation are discussed in further detail in US 2004/0077519A1 and US 2004/0097755A1. As used herein, the term "ionic liquid composite" refers to a mixture of a salt (which can be solid at room temperature) with a proton donor Z (which can be a liquid or a solid) as described in the patent documents immediately above. Upon mixing, these components turn into an ionic liquid that melts or flows at about 100°C or less, and the mixture behaves like an ionic liquid.

The ionic liquid useful in the present invention comprises a cationic component (i.e., components having a nitrogen or phosphorus heteroatom with substituents such that the
heteroatom is a "cationic center") selected from the group consisting of components having the following formulae:

AMMONIUM

PHOSPHONIUM

PYRIDINIUM

PYRIDAZINIUM

PYRAMIDINIUM

PYRAZINIUM

IMIDAZOLIUM

PYRAZOLIUM

OXAZOLIUM

1,2,3-TRIAZOLIUM

1,2,4-TRIAZOLIUM

THIAZOLIUM

QUINOLINIUM

ISOQUINOLINIUM

PIPERDINIUM

PYRROLIDINIUM
wherein the $R^1$-$R^8$ substituents are independently selected from the group consisting of H, Cl-C6 alkyl, alkenyl, hydroxalkyl, haloalkyl, alkoxyalkyl; C6-C10 aryl or C8-C16 alkylenearyl; and mixtures thereof, with the proviso that the cationic center heteroatom substituents not be H, i.e., the cationic center is a "hard quat."

The ionic liquid useful in the present invention further comprises an anionic component ("X"), which, when paired with the cationic component, forms the ionic liquid. The anionic component is selected from the group consisting of halogens, especially chloride or bromide, C1-C6 carboxylates, C1-C6 alkyl sulfates, mono- or di- Cl-CIO alkyl sulfosuccinates, mono- or di- Cl-CIO ester sulfosuccinates, and mixtures thereof.

In some embodiments, the ionic liquid has the formula:

$$\begin{align*}
\text{cation}^+ & \text{X}^- \\
\text{wherein } R^1 & \text{ are each independently selected from the group consisting of C1-C6 alkyl, alkenyl, hydroxalkyl, haloalkyl, alkoxyalkyl; C6-C10 aryl or C8-C16 alkylenearyl; preferably a C1-C6 alkyl moiety or a C1-C6 alkoxyalkyl moiety or wherein } R^1 \text{ can also be H; and the anionic component } X \text{ is as noted above. In a specific embodiment, the ionic liquid has the formula immediately above, wherein } R^1 \text{ is a C1-C6 alkyl moiety or C1-C6 alkoxyalkyl moiety, } R^2 \text{ is methyl and the anion is chloride.}
\end{align*}$$

In other embodiments, the ionic liquid has the formula:

$$\begin{align*}
\text{cation}^+ & \text{X}^- \\
\text{wherein } R^1-R^4 \text{ are each independently C1-C6 alkyl, alkenyl, hydroxalkyl, haloalkyl, alkoxyalkyl; C6-C10 aryl or C8-C16 alkylenearyl; and the anionic component } X \text{ is as noted above. In still other embodiments, the ionic liquid has a dioctyl sulfosuccinate anion and a cationic component as shown immediately above.}
\end{align*}$$

Other examples of ionic liquids that are useful in the present invention are described in US 6,048,388; US 5,827,602; US 2003/915735A1; US 2004/0007693A1; US 2004/003120; US 2004/0035293A1; WO 02/26701; WO 03/074494; WO 03/022812; and WO 04/016570.
Typically, ionic liquids have high viscosities (greater than about 1000 mPa-s) at room temperature. In some embodiments of the present invention, the ionic liquids or cocktails of ionic liquids, which are undiluted with adjuncts, co-solvents or free water, have viscosities of less than about 750 mPa-s, preferably less than about 500 mPa-s, as measured at 20°C. In other embodiments, the viscosity of undiluted ionic liquids or cocktails are in the range from about 0.1 to about 400 mPa-s, preferably from about 0.5 to about 300 mPa-s, and more preferably from about 1 to about 250 mPa-s.

The viscosities of the ionic liquids can be measured on a Brookfield viscometer model number LVDVII+ at 20°C, with spindle no. S31 at the appropriate speed to measure materials of different viscosities. Typically, the measurement is done at a speed of 12 rpm to measure products of viscosity greater than about 1000 mPa-s; 30 rpm to measure products with viscosities between about 500 mPa-s to about 1000 mPa-s; and 60 rpm to measure products with viscosities less than about 500 mPa-s. The undiluted state is prepared by storing the ionic liquids or cocktails in a desiccator containing a desiccant (e.g. calcium chloride) at room temperature for at least about 48 hours prior to the viscosity measurement. This equilibration period unifies the amount of innate water in the undiluted samples.

**BIOPOLYMER STARTING MATERIALS**

Biopolymers suitable for the sulfation or sulfonation process of the process include, but are not limited to, various oligo- and poly-saccharides. Nonlimiting examples of saccharides include starch, chitin, chitosan, dextran, maltodextran, dextrin, maltodextrin, gums, agar, alginites, and the like. Exemplary gums include xanthan gum, guar gum, locust bean gum and tamarind gum.

Suitable polysaccharides that are useful in the present invention include, but are not limited to, polysaccharides with a degree of polymerization (DP) over 40, preferably from about 50 to about 100,000, more preferably from about 500 to about 50,000, comprising one or more repeat units selected from the group consisting of saccharides containing 5 and/or 6 carbon atoms, including, but not limited to, mono- and di-saccharides such as isomaltose, isomaltotriose, isomaltotetraose, glucose, fructose, galactose, xylose, mannose, arabinose, rhamnose, maltose, sucrose, lactose, maltulose, ribose, lyxose, allose, altrose, gulose, idose, talose, trehalose, nigerose, kojibiose, lactulose; oligosaccharides, such as maltooligosaccharides, isomaltooligosaccharide, fructooligosaccharide, levoooligosaccharides,
galactooligosaccharide, xylooligosaccharide, gentiooligosaccharides; trisaccharides, 
 tetrasaccharides, pentasaccharides, hexasaccharides, oligosaccharides from partial hydrolysates 
of natural polysaccharide sources and mixtures thereof.

The polysaccharides may also include sugar alcohols as the repeat units. Nonlimiting 
examples of sugar alcohols include sorbitol, erythritol, arabinol, xylitol, threitol, pentaerythritol, 
mannitol and galactol and the like.

The polysaccharides can be linear, or branched in a variety of ways, such as 1-2, 1-3, 1-4, 1-6, 2-3 and mixtures thereof.

It is desirable, but not essential, that the polysaccharides of the present invention have a 
weight average molecular weight in the range of from about 10,000 to about 100,000,000, 
more preferably from about 50,000 to about 100,000,000, most preferably from about 100,000 to 
about 1,000,000.

PROCESSES

The present invention encompasses a method for preparing modified biopolymers. In a 
convenient mode, method comprises the steps of at least partially dissolving a biopolymer in an 
ionic liquid in its fluid state and in the substantial absence of water; adding a sulfation or 
sulfonation agent to convert the biopolymer into a modified biopolymer; and optionally adding 
a recovery solvent to the mixture, then separating the modified biopolymer from the mixture.

Due to the strong solvating power of the ionic liquid, the biopolymers, which are 
insoluble or have limited solubility in organic solvents or water, can be at least partially 
dissolved (usually at least about 1%, by weight) under mild conditions. For example, partial 
dissolution may be achieved even when no heat is applied. The term "partial dissolution" as 
used herein means the biopolymer would at the very least undergo some molecular or 
macromolecular changes, for example, decreased crystallinity, lowered glass transition 
temperature, disentanglement or disintegration of the molecular bundles, and the like. For 
some embodiments of the present invention, ever partial dissolution is found to activate the 
biopolymers sufficiently to allow the chemical modification to take place.

The dissolution step can be carried out at temperatures from about room temperature 
(20°C) to about 100°C under atmospheric pressure. In some embodiments, the dissolution 
process is carried out at temperatures from about 40 to about 90°C. Moreover, acid or base
additive is not required for the dissolution or partial dissolution step, but can be employed if desired. Optionally, higher temperatures (for example, up to about 130°C) may be employed to increase the dissolution rate, thus, reduce the processing time. The dissolution step may take from about 1 minute to about 5 hours, depending on the temperature.

For purposes of illustration, but not limitation, the amount of ionic liquids to biopolymers may have a weight ratio of from about 1:2 to about 100:1, or preferably from about 5:1 to about 50:1, or preferably from about 20:1 to about 10:1.

Under optimal conditions, the dissolution step produces a clear, transparent, or translucent solution or suspension (hereinafter referred to collectively as "solution") comprising the ionic liquid and the biopolymer, wherein the biopolymer is at a state of at least partially dissolved to completely dissolved.

In one embodiment, the dissolution mixture comprises from about 1 to about 15% or from about 5 to about 9% by weight of the solution of a biopolymer and at least about 50% by weight of the solution of an ionic liquid. Preferably, the solutions are substantially anhydrous.

The term "substantially anhydrous" as used herein means less than about 10 wt% of water is present, preferably less than about 5 wt% of water is present, and more preferably, less than 1 wt% of water is present.

The sulfating or sulfonating agent is added to the reaction mixture, typically with stirring over a time period of 1 minute to about 2 hours. After the addition step, the reaction mixture is allowed to react for about 1 minute to about 12 hours with stirring and gentle heating (up to a temperature of about 130°C). Optionally, sonication, pressure and/or vacuum may be applied to facilitate the reaction. If the reaction is exothermic, cooling may optionally be employed to maintain the desired reaction temperature.

Suitable agents for sulfation or sulfonation include, but are not limited to, chlorosulfonic acid, [SO₃ · pyridine] complex, sulfuric acid, sulfamic acid, SO₃, and the like. When a very reactive modifying agent such as chlorosulfonic acid is used, it is added to the reaction mixture slowly or dropwise, with stirring; since the reaction with the dissolved or partially dissolved biopolymer is almost instantaneous. The reaction is essentially complete when all the modifying agent is added. The amount of modifying agent is typically from about 1 to about 6 moles, or from about 2 to about 5 moles per mole of monomer unit of the biopolymer.
At the end of the reaction, the biopolymer is converted to a modified (sulfated, sulfonated, or mixed) biopolymer. A recovery solvent can then be added to the mixture to reduce the solvating power of the ionic liquid; thus, the modified biopolymer is rendered nonsoluble the reaction mixture. Then, the modified biopolymer is recovered by known separation methods, such as sedimentation, crystallization, centrifugation, decantation, filtration and combinations thereof.

The degree of substitution (DS) in the resulting modified biopolymer typically ranges from about 1 to about 6 moles, preferably from about 2 to about 4 moles of sulfate or sulfonate (or both) substituents per mole of monomer unit of the biopolymer.

In one embodiment, an effective amount of recovery solvent is added to the reaction mixture such that the modified biopolymer precipitates from the mixture. The weight ratio of recovery solvent to ionic liquid ranges from about 100:1 to about 1:2, preferably from about 20:1 to about 1:1, more preferably from about 10:1 to about 2:1. Optionally, acid or base can be added to the mixture to facilitate the precipitation and recovery of the biopolymers.

Exemplary recovery solvents include water, C1-C6 alcohols, C2-C6 ethers and acetone. Using water as the recovery solvent is particularly advantageous because no volatile organic solvent is involved and the entire process is conducted with environmentally friendly media.

In a further embodiment, the ionic liquid is recycled for re-use in the process or for other use(s). The recovery solvent can be separated from the ionic liquid by evaporation, distillation or drying over absorbents, the latter being quite useful when water is the recovery solvent. Suitable absorbents or absorbent materials include those materials capable of selectively ingesting (via absorption or adsorption) water without ingesting ionic liquid. Suitable absorbents include, but are not limited to, hydrogel forming absorbent polymers, absorbent gelling materials (AGMs), and mixtures thereof. Exemplary absorbent materials are disclosed in US 3,661,875; US 4,076,663; US 4,093,776; US 4,666,983; US 4,734,478; US 4,555,344; US 4,828,710; US 5,601,542; US 6,121,509; WO 99/34841; and EP 648,521 A2.

COMPOSITIONS CONTAINING MODIFIED BIOPOLYMERS

The modified biopolymers prepared according to the invention may be used in various applications and environments. For example, the modified biopolymers may be in combination
with other benefit agents or with functional components, such as detersive surfactants, enzymes, perfumes, bleaches, softeners and the like.

The modified biopolymers can be used in fabric care, surface care and air care compositions. These biopolymers may impart fabric appearance benefits to laundered fabrics, such as reduction of pills and fuzz, protection against color fading, improved abrasion resistance, and overall improved appearance. The modified biopolymers may also be used in fabric care and surface care composition to provide cleaning benefits.

The compositions containing the modified biopolymers according to the present invention may additionally include one or more conventional fabric, surface and/or air treating adjunct components, as desired. Suitable adjunct components include, but are not limited to, other surfactants and builders (such as silicas, zeolites, phosphates, polacrylates, poly(acrylic-maleic) copolymers), enzymes, enzyme stabilizers (such as propylene glycol, boric acid and/or borax), suds suppressors, soil suspending agents, soil release agents, other fabric treating benefit agents such as anti-abrasion agents, wrinkle resistant agents, stain resistant agents, and water resistant agents, flame retardants, antimicrobial agents, metal bleach catalysts, bleaching agents, softeners, anti-pilling agents, water repellant agents, ultraviolet protection agents, pH adjusting agents, chelating agents, smectic clays, solvents, hydrotripes and phase stabilizers, structuring agents, dye transfer inhibiting agents, sizings, perfumes, coloring agents and mixtures thereof. Additional examples of suitable adjuncts are disclosed in US 5,545,350, Baker et al.; US 6,090,767, Jackson et al.; US 6,420,326, Maile et al.; US 6,482,793, Gordon et al.; US 6,491,840, Frankenbach et al.; US 6,548,470, Buzzaccarini et al.; US 6,608,021, Westfield et al.; US 6,767,880, Foley et al.; and US 6,803,355, Panandiker et al.

The various optional adjunct ingredients, if present in the compositions herein, should be utilized at concentrations conventionally employed to bring about their desired contribution to the composition. Frequently, the total amount of such optional ingredients can range from about 0.01% to about 99%, preferably from about 0.1% to about 10%, and more preferably, from about 0.1 to about 5% by weight of the composition.

In another aspect of the present invention, the modified biopolymer may provide softening benefits and/or may improve delivery of another component or benefit agent to fabric surfaces in a substantive manner, i.e., to improve the deposition of such benefit agents on a fabric surface. Alternatively, or in addition, the modified biopolymers may assist in deposition
of benefit agents which are later released from a fabric surface in a controlled release or
delayed release manner. Exemplary benefit agents which may be used in association with a
modified biopolymer according to the invention include, but are not limited to, perfumes, dyes,
dye fixative agents, sizings, skin conditioning actives, vitamins, enzymes, surfactants,
antimicrobial agents, builders, chelants, bleaches, bleach catalysts, bleaching boosters, bleach
activators, softeners, suds suppressants, free radical initiators, ultraviolet protection agents,
wrinkle resistant agents, fire retardants, brighteners, and mixtures thereof.

Air care compositions typically contain at least one air care component, for example a
perfume, antimicrobial agent, or the like, in combination with a modified biopolymer according
to the invention.

The surface, fabric and/or air care compositions may be formulated in any suitable
form, including liquid, aerosol, gel, paste, foam, or solid. When the composition is in the solid
form, it can be further processed into granules, powders, tablets, or bars.

The composition may be employed as a component of another cleaning product, for
example by application to an absorbent substrate to provide a wipe for use in various
applications. Any suitable absorbent substrate may be employed, including woven or
nonwoven fibrous webs and/or foam webs. It is preferred that such an absorbent substrate
should have sufficient wet strength to hold an effective amount of the composition according to
the present invention to facilitate cleaning.

The compositions may also be provided in a unit dose product, which comprises the
composition and a unit dose package made of water soluble polymer film. Unit dose package
such as those disclosed in US 4, 973,416; US 6,451,750; US 6,448,212; and US
2003/0,054,966Al, are suitable for use with the composition of the present invention. The
embodiments containing little or no water (e.g., the "supercompact" composition) may be
advantageous for improving the stability of unit dose packaged materials and products.

The compositions may be provided in various forms, including, but not limited to, hand
dishwashing detergents, automatic dishwashing detergents, fabric pretreating compositions,
hand laundry detergents, automatic laundry detergents, and the like.

EXAMPLES

Example 1 - Sulfation of Dextran in Ionic Liquid
A mixture of dextran (Sigma, average molecular weight or MW about 19,500 Daltons, 0.5 gram, 0.0031 equivalents), 1-n-butyl-3-methylimidazolium chloride (12 grams) and pyridine (0.5 gram) is added to a 150 ml round bottom flask and held in a vacuum oven at 70°C overnight. The flask is then equipped with a magnetic stir bar, a condenser, and a gas inlet tube, and placed in a 75°C oil bath under argon. After a few minutes, the viscous mixture becomes stirrable and is stirred slowly by the stir bar. Powders of sulfur trioxide-pyridine complex (Aldrich, 0.5 gram, 0.0031 mol) are added. The powders slowly dissolve, resulting in a homogeneous light brown viscous mixture, which is allowed to react at 75°C with stirring for 4 hours. Then the mixture is cooled to room temperature, precipitated with about 50 ml of methanol and neutralized with sodium methoxide (Aldrich, 0.69 gram of 25% mixture in methanol, 0.0032 mol).

The crude product, a fine white precipitate, is isolated by suction filtration, washed with generous portions of methanol, and dried on a Kugelrohr apparatus (65°C at about 1 mm Hg for one hour) to yield 0.70 grams of the final product in the form of crunchy light brown solid. Carbon-13 NMR of the product shows the emergence of new peaks at about 77 ppm and about 80 ppm consistent with sulfation.

Example 2 - Sulfation of Carboxymethyl Dextran in Ionic Liquid

A mixture of 0.5 gram (about 0.0026 equivalents) of carboxymethyl dextran (wt. Avg. MW about 23,000 Daltons, Degree of Substitution or DS about 0.33), 12 grams of 1-n-butyl-3-methylimidazolium chloride and 0.5 gram of pyridine is added to a 250 ml round bottom flask and held in a vacuum oven at 70°C overnight. The flask is then equipped with a magnetic stir bar, a condenser, and a gas inlet tube, and placed in a 75°C oil bath under argon. After a few minutes, the viscous mixture becomes stirrable and is stirred slowly by the stir bar. Powders of sulfur trioxide-pyridine complex (Aldrich, 1.2 grams, 0.0078 mol) are added. The powders slowly dissolve in the mixture, resulting in a homogeneous light brown viscous mixture, which is allowed to react at 75°C with stirring for 4 hours. Then, the mixture is cooled to room temperature, precipitated with about 50-70 ml of methanol and neutralized with sodium methoxide (Aldrich, 1.7 grams of 25% mixture in methanol, 0.0080 mol).

The crude product, a fine white precipitate, is isolated by suction filtration, washed with generous portions of methanol, and dried on a Kugelrohr apparatus (65°C at about 1 mm Hg for one hour) to yield 1.4 grams of final product in the form of crunchy light brown solid. Carbon-
NMR of the product shows the emergence of new peaks at about 75 ppm and about 77 ppm consistent with sulfation.

Example 2 - Laundry Detergents

Non-limiting examples of laundry detergent compositions formulated to provide improved removal of particulate soils from fabrics (clay/carbon black) are as follows:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Range % (wt. of composition)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_{10}^{14} ) alkyl benzene sulfonate</td>
<td>0% - 25% * typically 1% - 20%</td>
</tr>
<tr>
<td>( \text{C}<em>{10}^{14} \text{C}</em>{2} ) alkyl ethoxy (EO(_{3-10})) sulfate</td>
<td>0% - 25% typically 3% - 20%</td>
</tr>
<tr>
<td>( \text{C}<em>{10}^{14} \text{C}</em>{20} ) alkyl sulfate</td>
<td>0% - 25% typically 1% - 20%</td>
</tr>
<tr>
<td>Ethoxylated ( \text{C}<em>{10}^{14} \text{C}</em>{18} ) alcohols</td>
<td>0% - 25% typically 3% - 20%</td>
</tr>
<tr>
<td>Zeolite builder</td>
<td>0% - 40% typically 10% - 25%</td>
</tr>
<tr>
<td>Sulfated dextrin **</td>
<td>0.01% - 20% preferred 0.1% - 1%</td>
</tr>
<tr>
<td>Miscellaneous ***</td>
<td>to 100%</td>
</tr>
</tbody>
</table>

* Total anionic surfactant is product should typically fall in the 5-25% range.

** According to the present invention; mole ratio of sulfate to saccharide unit approximately 0.5 : 1.

*** Auxiliary builders, optical brighteners, bleach, processing aids, moisture, perfume.

It should be understood that every maximum numerical limitation given throughout this specification includes every lower numerical limitation, as if such lower numerical limitations were expressly written herein. Every minimum numerical limitation given throughout this specification will include every higher numerical limitation, as if such higher numerical limitations were expressly written herein. Every numerical range given throughout this specification will include every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

All documents cited are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention. To the extent that any meaning or definition of a term in this written document conflicts with any meaning or definition of the term in a document incorporated by reference, the meaning or definition assigned to the term in this written document shall govern.
While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.
What is claimed is:

1. A method for preparing a modified saccharide-based biopolymer by the reaction of a sulfation or sulfonation agent, or mixtures thereof, with a saccharide-based biopolymer, characterized in that the reaction is conducted in a reaction medium comprising an ionic liquid.

2. A method according to Claim 1, comprising:
   (a) at least partially dissolving said biopolymer in an ionic liquid;
   (b) adding a sulfation or sulfonation agent to said biopolymer and converting the biopolymer into a sulfated or sulfonated biopolymer.

3. The method according to claim 1 wherein the sulfation or sulfonation agent is selected from the group consisting of chlorosulfonic acid, $\text{SO}_3 \cdot \text{pyridine complex}$, sulfuric acid, sulfamic acid, $\text{SO}_3$, and mixtures thereof.

4. The method according to claim 1 wherein the biopolymer is a saccharide selected from the group consisting of starch, chitin, chitosan, dextran, maltodextran, dextrin, maltodextrin, gums, agar, alginates, and mixtures thereof.

5. The method according to Claim 1 wherein the ionic liquid comprises a cationic component including a heteroatom having substituents such that the heteroatom is a cationic center, said cationic component being selected from the group consisting of components having the following formulae:
wherein the $R^1$-$R^8$ substituents are independently selected from the group consisting of H, C1-C6 alkyl, alkenyl, hydroxyalkyl, haloalkyl, alkoxyalkyl; C6-C10 aryl or C8-C16
alkylenearyl; and mixtures thereof, with the proviso that the substituents at the cationic center not be H; and
an anionic component selected from the group consisting of halogens, C1-C6 carboxylates, C1-C6 alkyl sulfates, mono- or di- Cl-ClO alkyl sulfosuccinates, mono- or di- Cl-ClO ester sulfosuccinates, and mixtures thereof.

6. The method according to claim 1 further comprising the steps of adding a recovery solvent and separating the modified biopolymer.

7. The method according to claim 7 wherein the recovery solvent is selected from the group consisting of water, C1-C6 alcohols, C2-C6 ethers, acetone, and mixtures thereof.

8. The method according to claim 7 further comprising the step of recycling the ionic liquid for re-use.

9. A fabric care composition, characterized in that it comprises at least one sulfated or sulfonated biopolymer produced according to the method of claim 1, and at least one additional fabric care component.

10. The fabric care composition of claim 9, wherein the fabric care component is selected from the group consisting of perfumes, dyes, dye fixative agents, sizings, skin conditioning actives, vitamins, enzymes, surfactants, antimicrobial agents, builders, chelants, bleaches, bleach catalysts, bleaching boosters, bleach activators, softeners, suds suppressants, radical initiators, ultraviolet protection agents, wrinkle resistant agents, fire retardants, brighteners, and mixtures thereof.