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Detergency Mechanisms and Cellulosic Surfaces: A Review

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The release of soils and impurities from cellulosic surfaces plays a critical role in such processes as the laundering of clothes and the deinking of wastepaper pulps. This article reviews publications that provide evidence about factors that affect such release and the mechanisms by which such factors operate. In general, cellulosic substrates provide advantages for the release of contaminants due to their hydrophilic nature and due to their permeability, allowing the transport of surfactants to contact interfaces with dirt. However, the same permeability of cellulosic material also provides opportunities for contaminants to work themselves into internal crevices and pores, from which they are difficult to remove. The article also reviews aspects of theory related to detergency and how those theories relate to the laundering, deinking, and purifying of substrates based on cellulose and related plant materials. Cellulose and some of its derivatives also can play a role in detergent formulation, especially as builders or as finishes placed on textile surfaces, which sometimes aid in the release of dirt.

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INTRODUCTION

The premise of this article is that various characteristic properties of cellulosic materials, such as cotton, rayon, and cellulosic pulp fibers, will have notable effects on the needed formulation and the efficiency of detergent systems and process conditions leading to their efficient cleaning. A detergent can be defined as a formulation that includes a surface-active compound, together with other ingredients, to promote the release of dirt and other contaminants. The main focus of this article is aqueous media. Though laundering has attracted the most research related to detergency, such studies are also relevant for the de-inking of wastepaper, the washing of freshly pulped cellulosic fibers, and other potential technologies aiming to purify cellulose-based materials.

Laundering is big business. It is an unusual business with respect to where most of the automated processing occurs – right within the households of modern citizens. It has been estimated that approximately one hundred billion dollars of detergents will be used per year in the world by 2028 (GlobeNewswire 2022), of which about 44 billion dollars of it will be powder-type detergents. Given the immense scale of the usage of detergents, it is important to focus on such issues as the efficient action of detergents, factors affecting the release of dirt, and efforts to decrease environmental impacts. For example, it has been estimated that the energy required for a typical laundering cycle can be reduced by a factor of 2.5 by decreasing the washing temperature from 50 to 20 °C (Schmitz and Stamminger 2014). The development, over recent decades, of systems capable of washing clothes at lower temperatures can be counted as a great achievement, both in theoretical and practical terms (Phaodee *et al.* 2019). Despite such progress, there has been a continuing need for better understanding of the mechanism underlying detergency and for more clarity of the factors affecting the release of dirt. In this article, the work "dirt" will be used to denote a broad range of dirty substances, including both solid-like and liquid-like matter.

Various aspects of detergency have been covered in earlier review articles. Table 1 lists such reviews, calling attention to their primary focus. The existence of these review articles can help to justify the focus of the present article on detergency phenomena related to cellulose-based substrates.

Table 1. Published Review Articles Dealing with Detergency

Wetting and detergency	Kissa 1981
Detergency: Theory and technology	Cutler & Kissa 1987
Physical aspects of detergency; colloidal chemistry	Carroll 1993
Solubilization emulsification mechanism of detergency	Miller & Raney 1993
Polymer-surfactant interactions in detergent systems	Goddard 1994
Particle adhesion and removal	Visser 1995
Detergency: Its main mechanisms	Herrera 1996
Soaps and detergents: A theoretical and practical review	Spitz (ed.) 1996
Handbook of detergents: Properties	Broze 1999
Microscopy to define soil, fabric, and detergent characteristics	Obendorf 2004
Surfactant adsorption at the hydrophilic solid-water interface	Paria & Khilar 2004
Evolution of anionic surfactant technology for laundry	Scheibel 2004
Formulation of color-care and heavy-duty detergents	Oakes 2005
Science of detergency and washing	Kim 2008

To provide context for such a discussion, focusing on cellulose-based substrates, certain background is provided in the next section. Thus, some essential information about the following topics will be reviewed, with reference to sources with more details: cellulosic surface, surfactants, buffers and salinity, builders, enzymes, bleaches, bio-based detergent systems, characteristics of the dirt often present on cellulose-based surfaces, and typical laundering techniques.

TECHNICAL BACKGROUND

Definitions

Table A (in the Appendix) provides a list of terms used in the field of detergency. Readers who are new to this field might choose to study the list first, before continuing. Of particular interest are some terms related to mechanistic interpretations of detergency. The term "roll-up" merits some priority attention, since it pertains to a mechanism that is believed to be important for hydrophilic surfaces, such as cellulosic surfaces (Dillan *et al.* 1979; Miller and Raney 1993). One can envision a monolayer of surface-active agent rolling up and separating from the substrate that is being cleaned, thus causing oily or particulate dirt to be released. A contrasting term, snap-off, refers to a mechanism that more often has been applied to explain the release of oily dirt from relatively hydrophobic surfaces (Miller and Raney 1993). Entries in Table A are listed in alphabetical order.

Cellulosic Surfaces

The chemistry and physical structure of cellulose and its fibers have been described in detail elsewhere (Fengel and Wegener 1984), so only relevant highlights will be provided in this section. Briefly stated, cellulose can be escribed as a linear polymer comprised of glucose units. The regularity, simplicity, and the detailed structure of the cellulose chain favor a high degree of crystallinity in the natural polymer (*e.g.* about 65 to 85%), regardless of its plant source.

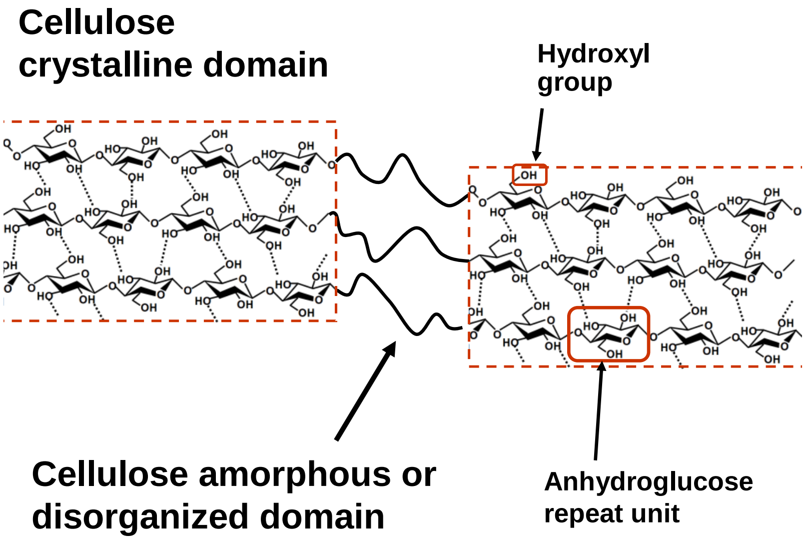

Fig. 1. Schematic depiction of the intermittent crystalline nature of cellulose. The fine dotted lines (in black) indicate that organized hydrogen bonds are present within and between the cellulose chains

Cellulose has three hydrophilic –OH groups per repeat unit, when considering anhydroglucose as the repeat unit (French 2017); however most of those –OH groups will be involved in highly regular intra- and inter-chain hydrogen bonding, which contributes to cellulose's non-solubility in most solvents and its intermediate affinity with water. Figure 1 emphasizes the intermittent crystallinity of cellulose (Nishiyama *et al.* 2003).

When it is obtained from trees, the cellulose is accompanied by hemicellulose and lignin (Fengel and Wegener 1984). The hemicellulose consists of relatively short copolymer chains comprising at least two types of either five-carbon (pentose) or six-carbon (hexose) groups connected by glycosidic bonds. The irregular nature of hemicellulose provide it with an amorphous (non-crystalline) nature. The lignin can be described as a random, moderately cross-linked copolymer comprised of phenol-propane units, giving it a relatively rigid and hydrophobic character. Kraft pulping, a treatment of wood chips with concentrated NaOH and Na_2S under pressure, is intended to remove some or most of the lignin (Fardim and Tikka 2011). Cotton, which is one of the main cellulosic materials used in textiles, is almost completely comprised of cellulose; relatively small amounts of wax on raw cotton fibers are often removed in the course of its processing (Easson *et al.* 2018). Though the content of wax in cotton is minor, its presence near the surface of the fibers means that it can have a disproportionate effect on such processes as laundering. For instance, Ginn *et al.* (1961) found that the adsorption of surfactant was primarily determined by the wax content of the cotton. The waxy materials, if still present in cotton cloth, also can be expected to favor the adhesion of oily dirt. Figure 2 shows the structure of waxy material that has been found on the surfaces of raw cotton fibers (Schmutz *et al.* 1994).

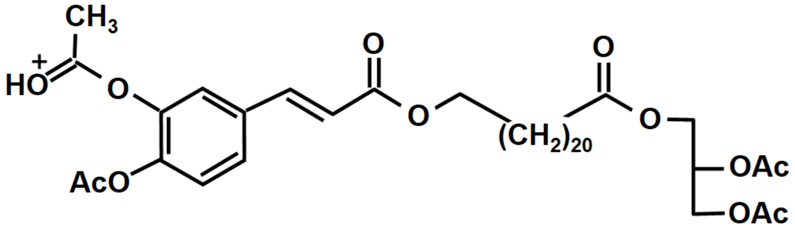

Fig. 2. Reported structure of a waxy compound found on cotton fibers

Likewise, regenerated cellulose fibers, such as rayon (viscose) and lyocell are essentially pure cellulose, though the chemistry may have been modified by chemical derivatization or surface treatment (Sayyed *et al.* 2019).

In contrast to some other types of fibers used in textile products, cellulose-based fibers, during laundering, can be envisioned as being a water-infused molecular structure. In addition to the water present between the fibers and in the fiber lumens, the swellability of the cellulose will bring water into the mesopores within the cell walls. Water also can be expected to diffuse into and to saturate the non-crystalline regions of the cellulose as well as any hemicellulose domains. In principle, the water that is able to penetrate into these regions also can allow access to alkalinity, some surfactant molecules, and possibly some enzymes, depending on accessibility. Thus, the characteristics of the cellulosic materials offer potential pathways for detergent components to reach interfaces between dirt and substrate, thus being able to influence the washing process.

Easier release from cellulose-based substrates

Several studies have reported easier release of soils from cellulose-based substrates in comparison to various synthetic polymers used in textiles. For example, Kissa (1981) reported much faster and more complete release of soil from cotton in comparison to either nylon of polyester fabrics, when subjected to the same detergent conditions and mild agitation. Likewise, Gotoh (2005) reported that removal efficiency of oily contaminants was higher for cellulose acetate in comparison with nylon and polyethylene in the presence of surfactant and variable amounts of ethanol. Tanthakit *et al.* (2008) stated that detergency was observed to be more effective with increasing hydrophilic character of the tested fabric. Thus, cotton items were found to be the cleanest after laundering, and polyester was the least clean. Reasons to help explain such differences will be considered in this article.

Ion exchange capacity

An inherent characteristic of most cellulosic materials is an ability to bind with positively charged ions, *e.g.* divalent metal ions such as Ca^{2+} (Lambert 1950; O'Connell *et al.* 2008; Hubbe *et al.* 2011, 2012). It is well known that increased water hardness, *i.e.* increased concentration of Ca^{2+} and Mg^{2+} in solution, tends to make it more difficult to wash clothes (Tanthakit *et al.* 2009; Gotoh and Mei 2017). The fact that cellulosic materials are able to bind hardness ions can be viewed in various perspectives. On the one hand, addition of purified cellulosic material to water will tend to reduce the hardness of the water, due to adsorption. On the other hand, cellulose-based articles, after their usage, are likely to remain partly saturated with hardness ions, which have potential to function as binders for various contaminants. As indicated in Fig. 3, the term "builder" often refers to a component of a detergent formulation that has the ability to bind hardness ions.

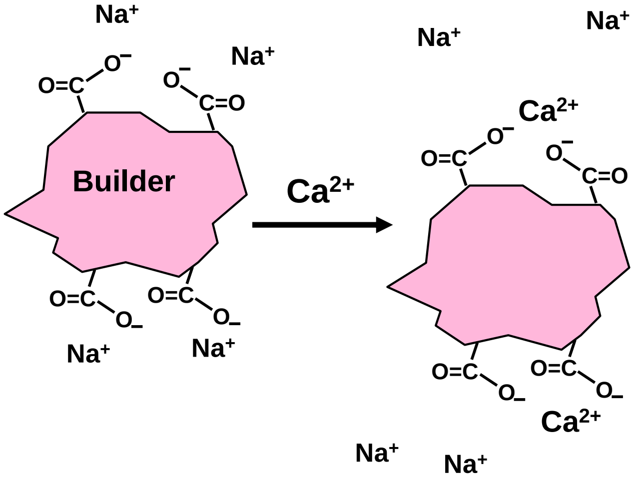

Fig. 3. Schematic depiction of a builder to be used in a detergent formulation and its ability to sequester hardness ions by an ion exchange process

Cotton

Cotton is a natural form cellulose that can be readily spun into yarns that can be woven into cloth for textile products. Like wood fibers, cotton fibers have a multilayer structure (Li and Hardin 1998). Cotton fibers have only a relatively small lumen space in the fiber's center, leading to high overall density. In principle, such a dense construction is expected to provide stiffer fibers that are less conformable in their wet state, compared for instance to a kraft pulp fiber from wood. Minor non-cellulose components of cotton include wax, pectic compounds, and proteins (Li and Hardin 1998).

The properties of cotton can be markedly changed by a process called mercerization (Grancarić *et al.* 1997; Obendorf 2004). This process involves treatment with moderately concentrated NaOH, which greatly swells the material. For instance, Stana-Kleinschek *et al.* (1990) employed a 24% solution of NaOH at 15 °C for 60 s to mercerize cotton. By temporarily dissolving the cellulose macromolecules, mercerization results in a transformation from the cellulose I to the cellulose II crystal form, usually with a lower degree of crystallinity. This transformation is illustrated in Fig. 4.

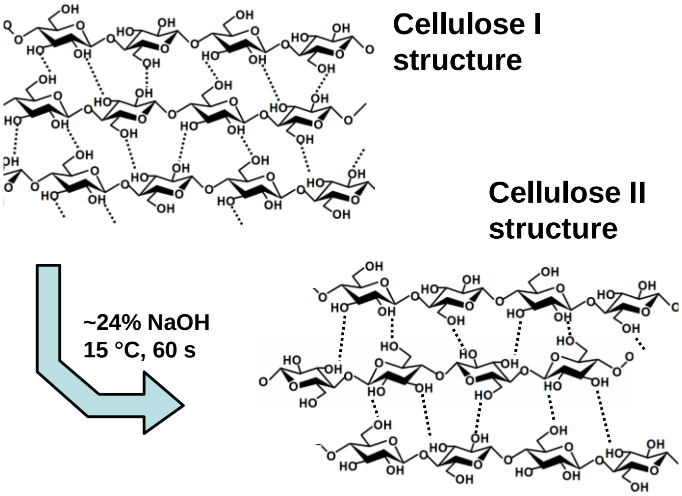

Fig. 4. Reversal of the direction of 50% of the cellulose chains during transformation from cellulose I to cellulose II in the course of mercerization

Another effect of the mercerization of cotton is that the lumen becomes less prominent, and the fiber surface becomes smoother (Stana-Kleinschek *et al.* 1999; Obendorf 2004). Grancarić *et al.* (1997) reported that mercerization increased the magnitude of the negative zeta potential of cotton threads, also leading to a higher ability to adsorb positively charged substances. Stana-Kleinschek *et al.* (1999) reported that mercerized cellulose tended to have a greater absorption of moisture and to be more accessible to dye molecules.

Regenerated cellulose

The popular textile fibers rayon (viscose) and lyocell are examples of regenerated cellulose. The term means that the cellulose had been completely dissolved, then precipitated out of solution in the process of returning to the solid phase. The processes for the two types of regenerated cellulose production are shown in Fig. 5. Regeneration processes result in some key differences relative to the starting material. Most importantly, the fibers can be produced as continuous filaments, and the surfaces are often quite smooth. Gotoh *et al.* (2015) noted, however, that rayon fibers can be sufficiently porous or rough such that particulate dirt can become entrapped in crevices. Penford *et al.* (2007) observed that the ability of regenerated cellulose to absorb cationic surfactant was much higher than that of the default cellulose surface prepared by monolayer deposition onto a silica substrate.

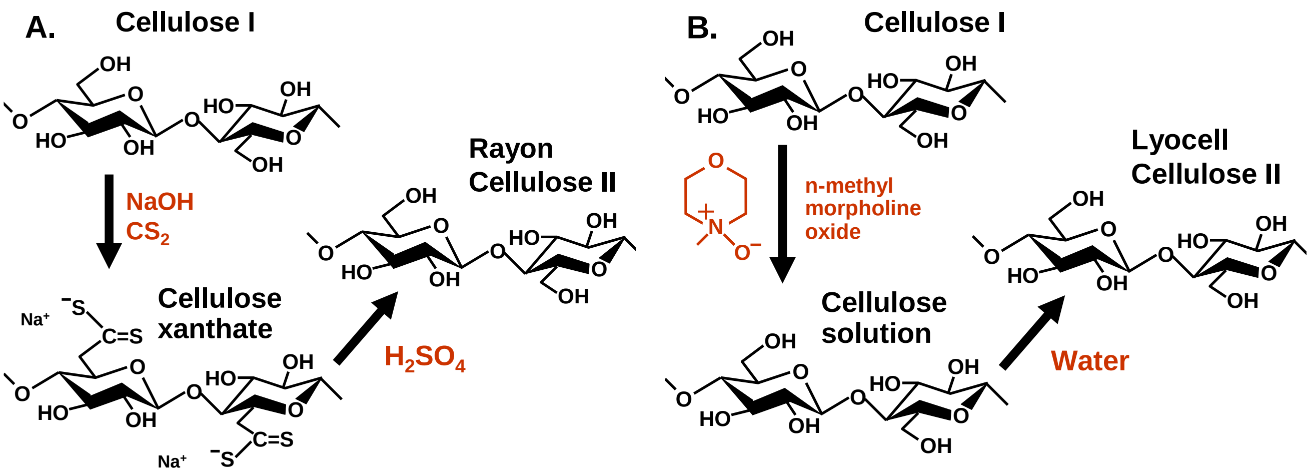

Fig. 5. Processes by which ordinary cellulose is formed into a solution, drawn into filament form, then returned to cellulose, but as a different crystal form and morphology; A: Viscose (xanthate rayon) process; B: Lyocell (n-morpholine oxide) process

Finishes on yarns and fabrics

The surface nature of textile fibers, regardless of their main composition, can be markedly changed by a process called finishing or sizing. Such processes usually involve passing a yarn or filament through a solution or suspension, allowing it to pick up some material that becomes dried onto its surface. For example, Higgins *et al.* (2003) studied various changes resulting from the application of a wrinkle-resistant finish onto plain woven cotton fabrics. Rhee *et al.* (1993a,b) tested the effects of finishing treatments aimed at stain-resistance and antistatic properties. In principle, a surface finish on a textile fiber has the potential to change its properties from hydrophobic to hydrophilic, thus rendering the fabric easier to launder. However, there can be ongoing concerns about the durability of such surface layers and their likely removal in the course of repeated laundering.

Surfactants

The key component of most common detergent systems is a surface-active compound, *i.e.* a surfactant. A surfactant generally can be described as having a hydrophobic “tail” group connected to a hydrophilic “head” group (Salager *et al.* 2017). The amphiphilic nature of such compounds helps them to draw various hydrophobic direct materials into an aqueous phase, often in the form of an emulsion or a stabilized suspended solid (Salager *et al.* 2022). Widely used surfactants in detergent formulations include anionic surfactants, nonionic surfactants, and extended surfactants. In addition, binary mixtures have been widely used, and research has been carried out with cationic surfactants (Salager *et al.* 2019).

Anionic surfactants

Surfactants having a negatively charged headgroup, *i.e.* the anionic surfactants, comprise the largest component, on average, of laundry detergents used in the US (Matheson 1996). Figure 6 shows two widely used examples. The headgroup is usually sulfonate or sulfate, both of which become fully dissociated over the whole pH range at which laundering takes place (Scheibel 2004; Ponnusamy *et al.* 2008; Budhathoki *et al.* 2016; Phaodee *et al.* 2020). Schott (1967) may have been the first to quantify the adsorption of surfactants (including sodium dodecyl sulfate) onto cellulose. The tail groups often include alkyl chains, such as the dodecyl group just mentioned. However, technologists have obtained superior detergency results when using products that include an aromatic group as well, *i.e.* dodecylbenzene sulfonate (Wingrave 1984; Cohen *et al.* 1992; Paria *et al.* 2004, 2005a; Samanta *et al.* 2004; Takahashi *et al.* 2007; Kalak and Cierpiszewski 2015; Gotoh *et al.* 2016; Gotoh and Mei 2017; Ou *et al.* 2021). Because most cellulosic surfaces have a weak negative charge (Hubbe *et al.* 2012), it is reasonable to assume that the anionic surfactants orient themselves with the tails facing outwards or lying down on the substrate, with the detailed orientation depending on the concentration in solution (Simoncić and Roman 2007).

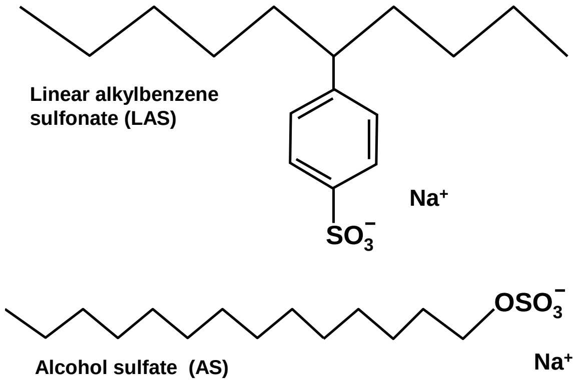

Fig. 6. Widely used anionic surfactant components for detergent formulations

Nonionic surfactants

Surfactants having an ethylene oxide chain as the headgroup constitute the major group of nonionic surfactants used in detergent formulations. The ratio of oxygen to carbon in the $–CH_2CH_2O–$ repeating unit is high enough to achieve complete solubility of ethylene oxide in water. Furthermore, ethylene oxide segments can be attached to a variety of hydrophobic groups, including propylene oxide, to make a range of useful surfactants. However, as noted by Miller and Raney (1993), the ethylene oxide groups are less hydrophilic than the anionic groups just considered. The fact that those groups do not interact with hardness ions such as Ca^{2+} can be regarded as an inherent simplification, relative to the use of anionic surfactants in detergents. The nonylphenol ethoxylates have shown particular promise as components of detergent formulations (Dillan *et al.* 1980). Another class of nonionic surfactants used in detergents goes by the name of "ethoxylated alcohols" (Scheuing and Hsieh 1988). Polyoxyethylene sorbitol esters, though they are widely used in industry, are less often used in laundry detergent formulations (Seo *et al.* 2011).

The fact that some surfactants work better than others, often depending on temperature and ionic conditions, is important in terms of formulation and when one is attempting to determine the mechanisms of action. Figure 7 shows two examples of nonionic surfactants (Matheson 1996). However, there is a serious limitation on using ethoxylated nonionics in household formulations due to 1,4-dioxane formation during the ethoxylation reaction. Accordingly, biobased alternatives such as alkylpolyglycosides are being used in several cleaning formulations in Europe and the US (Ortiz *et al.* 2022).

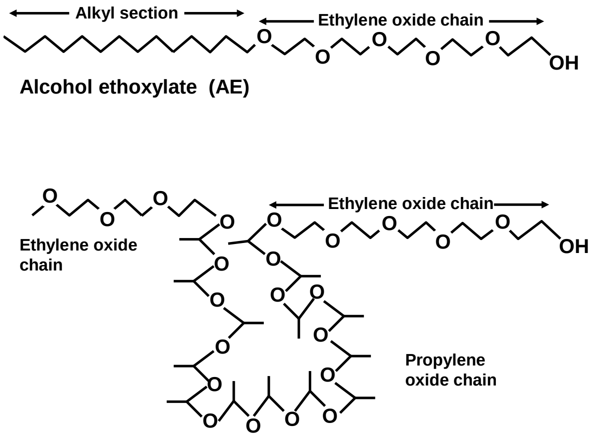

Fig. 7. Examples of nonionic surfactants

Extended surfactants

An extended surfactant can be briefly described as a surfactant that has a few propylene oxide groups or ethylene oxide groups (having intermediate polarity) interposed between the hydrophilic headgroup and the hydrophobic tail (Salager *et al.* 1979; Matheson 1996; Do *et al.* 2015; Salager *et al.* 2019). Compared to conventional surfactants, extended surfactants have been found to be more effective in the formation of microemulsions. Moreover, these microemulsions have been found to have much higher capacity to solubilize oil and to promote much lower interfacial tension (Dillan *et al.* 1979; Miñana-Perez *et al.* 1995; Kaewpukpa *et al.* 2008; Witthayapanyanon *et al.* 2008; Phan *et al.* 2010; Acosta *et al.* 2012; Hammond and Acosta 2012; Budhathoki *et al.* 2016; Attaphong and Sabatini 2017; Chanwattanakit and Chavadej 2018; Salager *et al.* 2019). This ability to form very small phase entities implies that the extended surfactants are able to achieve very low interfacial tensions. It appears that the groups of intermediate affinity (*i.e.* the ethylene-oxide segments), placed in the middle of this class of surfactant, increase the effectiveness of the extended surfactants in detergency. Two examples of extended surfactants (Matheson 1996; Witthayapanyanon *et al.* 2008) are shown in Fig. 8. Due to their limited biodegradability, however, such extended surfactants are not regarded as the most suitable for laundry detergents (Salager *et al.* 2022).

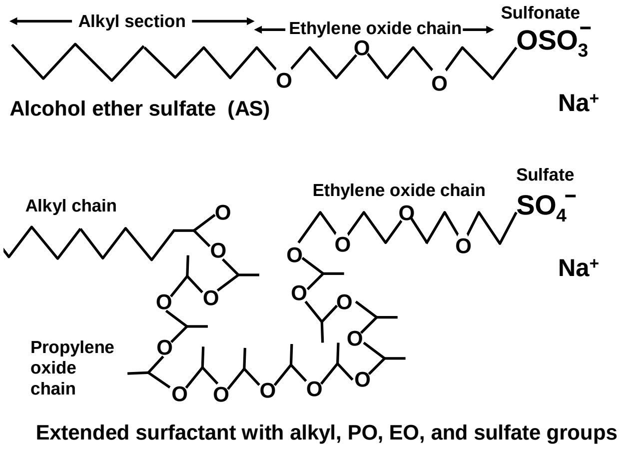

Fig. 8. Schematic examples of extended surfactants

Cationic surfactants

Due to their ability to interact strongly with the negatively charged carboxylate groups present on cellulosic surfaces, cationic surfactants have attracted a lot of research attention for such systems. The orientation often has been described as "head facing the substrate" (Alila *et al.* 2005; Paria *et al.* 2005b). Evidence in favor of such an orientation includes findings of increased hydrophobic character, especially at low to moderate dosages of surfactant (Syverud *et al.* 2011). Further evidence consists of the release of counter-ions (*e.g.* Cl^-) into the bulk solution upon adsorption of the cationic surfactant onto cellulose surfaces (Alila *et al.* 2005, 2007). At higher concentrations of cationic surfactant, double-layers can be expected; the second layer adsorbs with its tails facing or intertwining with the first layer, and the headgroups are left facing the aqueous solution (Muller *et al.* 1998). Patches of such double-layers of adsorbed cationic surfactant are referred to as admicelles (Alila *et al.* 2005). Notably, such double-layer structures will present a hydrophilic surface towards the aqueous phase. Cationic surfactants are used extensively as fabric softeners, which can be applied during the drying process (Pucha 1984).

Hydrophobic interactions

A tendency of the tail groups of surfactants to associate into tight films has been attributed to a hydrophobic effect (Tanford 1980; Hubbe *et al.* 2020). The driving force for such association is the relatively high energy of hydrogen bond interactions in aqueous systems. By self-organizing the hydrophobic entities such that they are pressed together, the system maximizes the amount of hydrogen bonds that can be formed. Figure 9 depicts some of the common ways in which surfactant molecules (using a linear alkyl sulfonate, *etc.*, as an example) in various forms that decrease the extent of blockage of hydrogen bonding within the system as a whole. Biswas and Chattoraj (1997) and Penford *et al.* (2007) found evidence of self-association between the hydrophobic tails of a cationic surfactant (hexadecyl trimethyl ammonium bromide), such that the molecules were present as hemimicelles, *i.e.* condensed patches of the cationic surfactants adsorbed as single monolayers. Woods *et al.* (2011) found related evidence in a mixed surfactant system with a combination of the same cationic surfactant as used in the other cited studies, but in combination with a nonionic surfactant. It will be assumed in this article that such interactions play an important role in detergency.

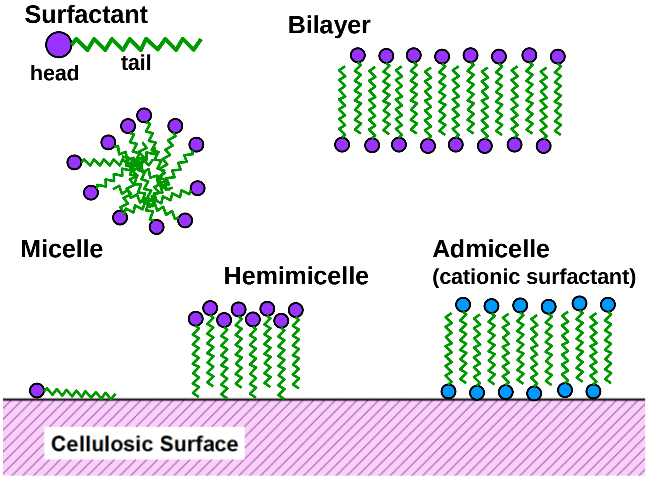

Fig. 9. Idealized depiction of ways of association among surfactant molecules in aqueous systems

Surfactant adsorption

It is proposed that "elbowing" is a useful analogy when thinking about the likely action of surfactants as they work to release dirt from surfaces during laundering. The effectiveness of the additive may depend on its ability to push things out of its way and make space for itself, thereby opening up a space between dirt and a textile fiber. It follows that the affinity of the surfactant for the interfacial region will play a key role. The energy associated with adsorption can be summarized by focusing on three categories of interactions – with the solid surfaces, with the water, and the self-association – as just considered above.

The tendency of surfactant molecules to form monolayers at surfaces is closely related to their tendency to form into micelles. There can be a close relationship between the critical micelle concentration (CMC) and the concentration at which a maximum adsorption at surfaces has been observed (Ginn *et al.* 1961; Biswas and Chattoraj 1997). The cited authors found many cases in which specific affinity of the surfactant for substrate led to a critical concentration for maximum adsorption that lay below the CMC. Paria *et al.* (2005a) proposed that the maximum is associated with the formation of hemimicelles, which can be regarded as patches of self-associated surfactant molecules oriented tightly at the surface. It has been proposed that the removal of dirt from a surface can be similar in principle to the formation of an emulsion (Kalak and Cierpiszewski 2015). Thus, as a first approximation, when the conditions for emulsification are better, one can expect that removal or dirt will be more effective. A later section of this article will consider Winsor conditions at the optimization of detergency.

Cloud point of a surfactant

To carry the elbowing analogy a step further, one can expect that more persistent and pushy commuters will be the most successful in getting into and out of packed subway cars. The situation can be compared to that of a surfactant that wants badly to get out of the bulk phase of solution. The cloud point refers to surfactant-oil-water systems that are formulated with nonionic surfactants. Technologists have long been aware that surfactant systems are often the most effective when they are somewhat higher than the cloud point, which represents the temperature above which they precipitate out of solution (Raney *et al.* 1987; Miller and Raney 1993).

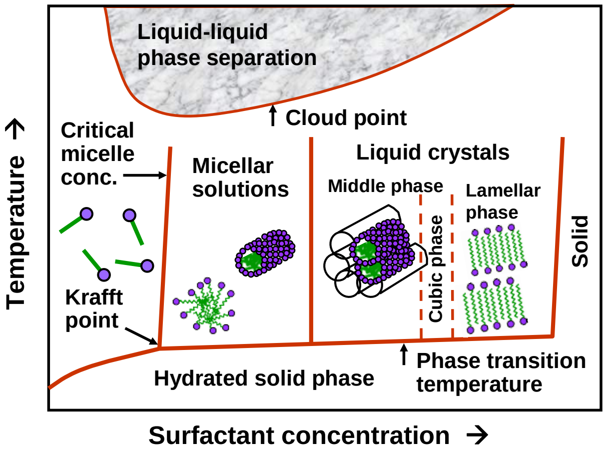

Fig. 10. General temperature-concentration plot for phases in aqueous surfactant mixtures

For instance, Borchart (1994) observed greatest effectiveness of deinking operations at temperatures somewhat higher than the cloud point. Kalak and Cierpiszewski (2015) estimated that the best detergency was obtained when only about 87 to 92% of the surfactant could be dissolved in the studies systems. Figure 10, based on a version by Nakama (2017), shows the location of the cloud point temperatures on an idealized plot of temperature *vs.* surfactant concentration.

Foam potential

The generation of foam is often taken as a clue by consumers as to the effectiveness of detergent action. Indeed, the ability of surfactants to lower interfacial tensions can be a factor in the stabilization of foam bubbles (Pugh 1996). Another factor important for foam stabilization in aqueous systems is the presence of water-soluble polymers, which can contribute to increased elasticity of bubble walls. Karthick *et al.* (2018) found that different classes of surfactants used in detergent formulations had different foaming tendencies. Raney and Miller (1987) found that the calcium salt of oleic acid functioned as a defoaming agent in such systems. The calcium oleate appeared to disrupt the surfactant monolayer structure, thus causing the bubbles to be less persistent.

Surfactant toxicity

In view of the need for more eco-friendly laundering systems, the toxicity of surfactant compounds can be important. Warne and Schifko (1999) found large differences in toxicity for different surfactant types. Scheibel (2004) reported the evolution of anionic surfactant technology over the passage of time, such that it currently tends to employ more eco-friendly options than in the past. A recent review by Ortiz *et al.* (2021) describes a trend toward the usage of bio-based surfactants, which in many cases have lower toxicity. In addition, as described in the cited article, new regulations related to dioxane are motivating growth in the marked of narrow-range ethoxylates having ultra-low dioxane levels.

Buffers and Salinity

It is tempting to underestimate the importance of aqueous ionic conditions, including the pH and buffering capacity, when thinking about the formulation of a detergent system. According to Matheson (1996), almost the opposite is true in the formulation of some industrial detergent systems. Such systems often place main reliance on the use of higher pH values, higher temperatures, and the use of bleach. The usage of surfactants in some industrial washing systems is minimal. Because of the relatively uniform operations of household washing machines, one may get a false impression that pH, buffering capacity, and salinity are not potent tools for achieving detergent effects.

By mass, sodium carbonate is often the first or second most prominent ingredient in a common laundry detergent formulation, often exceeding the amount of surfactant (Schwuger and Smulders 1987; Matheson 1996). The cited sources mention a combined range of about 5 to 30% of sodium carbonate in traditional and so-called high-density detergent formulations. Sodium carbonate can be described as a safe and relatively inexpensive agent for moderately increasing and buffering the pH in an alkali range. The high pH tends to convert insoluble calcium salts of fatty acids – a common form of soiling – into water-soluble sodium salts, which is a form of saponification (Gotoh 2005). The general reaction is outlined in Fig. 11. As shown, the alkalinity released upon dissolution of the sodium carbonate in water can convert insoluble calcium compounds into emulsifiable sodium compounds. Also shown is a sodium docecylsulfate (SDS) molecule, serving as an example of an anionic surfactant that could be used with the sodium carbonate in a detergent formulation.

Burkinshaw and Anthoulias (1997) found that a concentration of 5 g/L or sodium carbonate was sufficient to remove excess reactive dye after coloring cellulosic fibers, even in the absence of a surfactant. Follow-up work by Burkinshaw and Katsarelias (1997) showed that the addition of sodium carbonate rendered five different surfactants more effective in the removal of excess reactive dyes. Gotoh (2010) observed that increasing the pH aided the release of various soil types from both cotton and polyester. Dillan *et al.* (1979) attributed the effectiveness of sodium carbonate as a detergent component to its ability to provide soil particles with negative surface charges, due presumably to the dissociation of carboxylic acid groups on the surfaces.

$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH$$

$$NaOH + (RCOO)_2Ca \rightarrow 2RCOO^- Na^+ + Ca(OH)_2$$

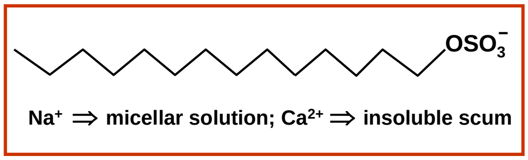

Fig. 11. Suggested role of sodium carbonate in converting insoluble calcium salts of fatty acids into their more soluble sodium forms

Salts, especially sodium sulfate, also have been shown to boost detergency in many cases, but the mechanism appears to be much different from that of sodium carbonate. As will be described in more detail later, the main role of sodium sulfate may be to fine-tune the effective size of anionic head-groups of anionic surfactants (Hammond and Acosta 2012). Powe (1963) found that inorganic salt addition tend to decrease the value of critical micelle concentration (CMC) of anionic surfactants, which is considered to be beneficial. Whatever the reason, an optimum level of the salt addition often has been found to coincide with the lowest interfacial tension and the best detergency effects related to microemulsions (Aveyard *et al.* 1985; Tongcumpou *et al.* 2003a,b; Acosta *et al.* 2012; Phaodee *et al.* 2020). Azemar *et al.* (1993) found that the addition of salt made it possible to increase the effectiveness of detergents at lower temperatures. Additionally, Vera *et al.* (2020) found that the nature of the salt has important effects on the surfactant solubility, interfacial tension, and rheological properties. This may significantly affect detergency performance of anionic surfactants.

Water hardness, *i.e.* the presence of calcium and magnesium ions, is widely reported to have unfavorable effects on detergent performance (Tanthakit *et al.* 2009; Gotoh *et al.* 2016, 2017; Vera *et al.* 2020). As already mentioned, calcium salts of various fatty acids and other organic acids tend to be insoluble (Harwot and van de Ven 1997). In addition, the divalent ions can adversely affect the anionic surfactants, tending to make them precipitate (Gotoh *et al.* 2016). These issues call for the use of additives called builders, which are described next.

Builders

Water softening

A primary function of various builder components in detergent formulations is to mitigate the effects of water hardness. Several contrasting types of builders have been found to be effective (Schwuger and Smulders 1987). These include phosphates, acrylates, carboxymethylcellulose (CMC), and zeolites. The listed substances each are able to bind the calcium and magnesium ions in some way, making their concentration in solution appear to be lower.

Phosphates

Various phosphate compounds, especially sodium tripolyphosphate (STPP), are known to be effective for mitigating the effects of hardness ions (Powe 1963; Schwuger and Smulders 1987; Cohen *et al.* 1992; Leal *et al.* 1996; Phillips *et al.* 2001; Tanthakit *et al.* 2009). Leal *et al.* (1996) described STPP as having the smallest adverse environmental impact of various phosphate types considered, based on the concentrations that were needed. However, there has been a switch from phosphates to alternative builders due to environmental concerns (Matheson 1996). When wastewater that contains phosphates is discharged to waterways, it supports eutrophication (Awual 2019). Because phosphate is often a limiting factor in the growth of microbes in water, its addition to rivers, lakes, and the ocean should be minimized. Part A of Figure 12 depicts the main interaction whereby STPP binds calcium ions.

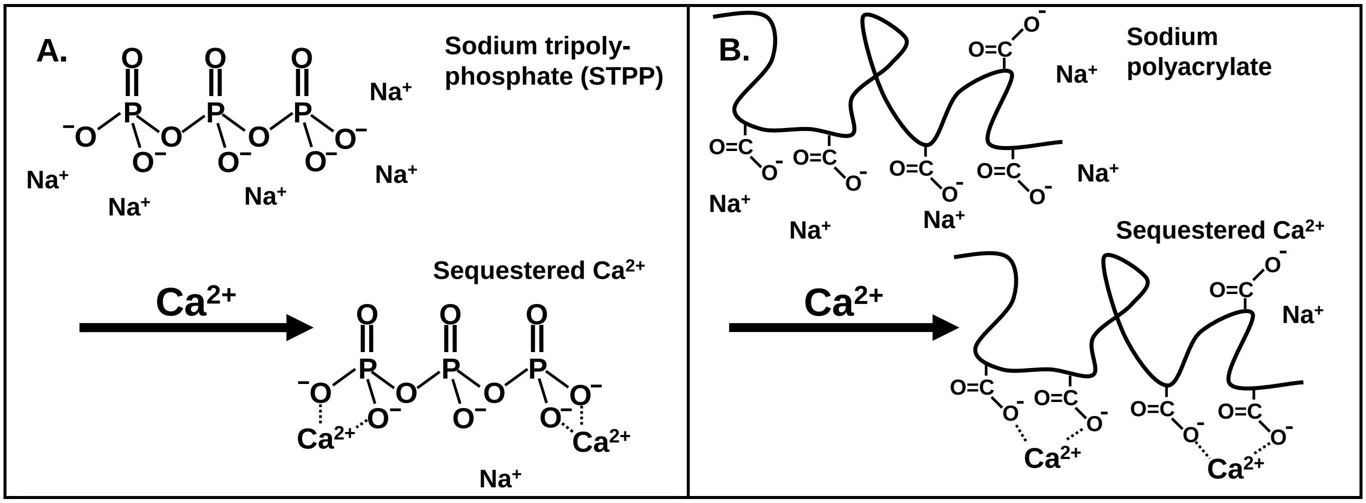

Fig. 12. Sequestration of hardness ions by (A) sodium tripolyphosphate (STPP) and sodium poly-acrylate. The dotted lines represent moderately stable chemical complexation.

Acrylates

Since the carboxylate ion is well known to bind divalent metal ions, especially when there are several of them close together in a compound, it is reasonable to consider carboxylated polymers as builders. Sodium acrylate and its copolymers have become widely used for that purpose (Schaffer and Woodhams 1977; Komaki *et al.* 2002; Milojević *et al.* 2013). The sequestration of hardness ions by sodium polyacrylate is depicted in Part B of Fig. 12. Milojević *et al.* (2013) found that the performance of such builders increased with increasing molecular mass up to 70,000 g/mole, after which there was no benefit of further increases in mass. Komaki *et al.* (2002) studied the ability of a certain type of polyacrylate to form complexes with fatty acid, which can be regarded as being unfavorable for laundering. According to Schaffer and Woodhams (1977), the acrylate polymers can have a superior binding ability for hardness ions in comparison to phosphates, but the acrylate polymers are not biodegradable.

Carboxymethylcellulose (CMC)

As a means to achieve the benefits of a polymer-based carboxylated builder, while attempting to minimize environmental problems, it makes sense to consider water-soluble polymers derived from cellulose. CMC is prepared from chemical-grade cellulose material by reaction of chloroacetic acid under strongly alkaline conditions with the formation of ether bonds (Rahman *et al.* 2021). When the degree of substitution (DS) becomes higher than about 0.4 per anhydroglucose unit, the material becomes increasingly soluble in water. Likewise, its ability to bind hardness ions increases with increasing DS. The biodegradability of CMC is evidenced by the fact that CMC is widely used in assays of the potency of cellulose-degrading enzymes (Chan *et al.* 2019). The effectiveness of CMC as a builder in detergent formulations has been reported (Vaughn and Smith 1948; Agarwal *et al.* 2012).

Microcrystalline cellulose (MCC)

Agarwal *et al.* (2012) tried something unusual. As an alternative to reacting microcrystalline cellulose (MCC) with chloroacetic acid under strongly alkaline conditions (to make CMC, as just described), they simply used the MCC itself in detergent formulations. Not only was the MCC effective, but it was judged to have performed better than then CMC used as a baseline. The MCC served as a thickener in a liquid detergent formulation. On the other hand, there is no reason to expect that ordinary MCC would affect the availability of hardness ions in aqueous solution, which is often regarded as a main job of builders. Some commercially available MCC products are coated with an adsorbed layer of CMC, which contributes to stability of their aqueous suspensions.

Zeolites

Zeolites can be described as microporous alumino-silicate crystalline materials that have huge internal capacity to bind various ions and small compounds. The complete regularity of their pore dimensions offer zeolites the potential to have very specific adsorption capabilities relative to the size of the adsorbate. A zeolite called Zeolite A has been found to be especially effective for the removal of hardness ions from solutions as part of detergent formulations. Figure 13 shows the crystal structure of Zeolite A, which contains two types of cage structure (Tanney 2017). Notably, the α-cage (supercage) structure appears well suited for accommodating the calcium ion.

Zeolites have been found to perform similarly to STPP (a phosphate compound) as a builder (Cohen *et al.* 1992; Matheson 1996; Phillips *et al.* 2001). In addition, zeolites do not contribute to the eutrophication of waterways after the discharging of treated wastewaters, as phosphates do (Matheson 1996). In fact, some positive effects of zeolites on health have been reported (Grancarić *et al.* 2009). Because of the solid particulate nature of zeolites, it is perhaps unsurprising that some of the solid material can remain with the textile products after laundering (Hurem *et al.* 1992). However, effects of the residual zeolite on the appearance and other properties of the laundered items were reported as being minor. An additional benefit of zeolites as that they may adsorb colorants that have been released from textiles (Kokol *et al.* 2018).

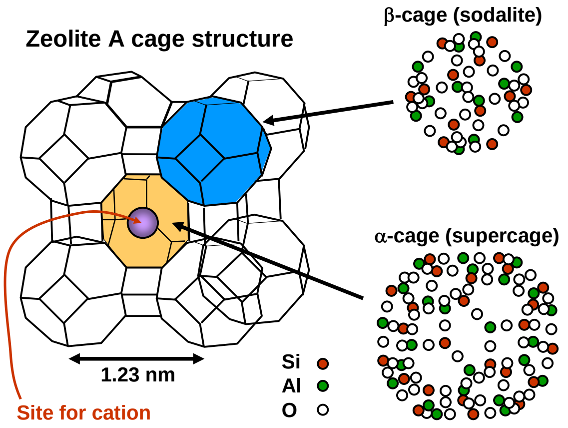

Fig. 13. Cage structure of Zeolite A (redrawn from original by Tanney 2017)

EDTA

Certain monomeric chelating agents, notably ethylenediaminetetraacetic acid (EDTA) and related chemicals, are known to be extremely effective for the binding of hardness ions and a range of other divalent metal ions. Such products can be effective as builders in detergent formulations (Eken-Saracoglu and Culfaz 1999; Tanthakit *et al.* 2009). However, chelating agents are seldom mentioned in literature related to detergency. Possible reasons may include the known lack of biodegradability of chelating agents (Pinto *et al.* 2014) and concerns about their environmental effects due to exceptionally strong binding of metal ions.

Fabric Softeners

The term "softening" can have a second meaning in addition to the binding of calcium and magnesium ions, as discussed above. The other usage refers to products that confer a softer feel to laundered items after they have been dried. Notably, it has been reported that such effects can be achieved by addition of bentonite to the detergent formulation (Carrion-Fite 2014). Presumably the effect is due to interruption of the bonding between filaments in the yarn as the material is being dried, thus favoring a fluffier, less dense structure that feels softer.

The conventional way to soften fabrics is to add certain cationic surfactants having optimized structures to the laundered items before the drying process (Pucha 1984; Matheson 1996; Levinson 1999; Murphy 2015). Some such agents are added during the rinsing stage of laundering (Levinson 1999; Murphy 2015), and often the material is added during the drying process. Quaternary ammonium compounds involving ester bonds, *i.e.* "ester quats," are now widely used, since they are readily biodegradable (Murphy 2015). Such fabric softeners, as shown in Part A of Fig. 14, have a family resemblance to the debonding agents that are sometimes used in papermaking when the goal is to achieve a bulkier, softer structure (Touchette and Jenness 1960; Conte and Bender 1992; Poffenberger *et al.* 2000). As was noted earlier, many cationic surfactants tend to adsorb as dense patches with their cationic groups facing a cellulose-based surface and their condensed monolayers of hydrophobic tails groups effectively preventing the development of hydrogen bonding between adjacent fibers or filaments of the fabric. This is shown, schematically, in Part B of Fig. 14. A reduction in inter-fiber hydrogen bonding means that the fibers within a cellulose-based textile material, after it has been dried, will slide easily relative to each other, thus decreasing the stiffness of the material. Tests of similar technology related to papermaking suggest that debonding agents will contribute to a softer feel of the dried item (Pawlak *et al.* 2022).

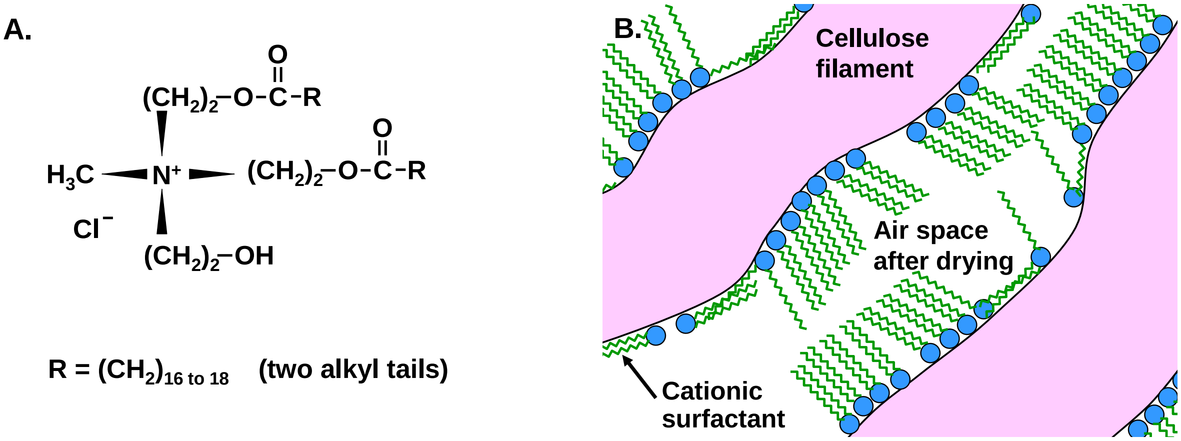

Fig. 14. Example of a fabric softener (ester quat type) (A) and its possible orientation on cellulose-based filaments after drying (B), leading to the inhibition of intra-fiber hydrogen bond formation

Enzymes

To supplement efforts aimed at the detachment of dirt, it can make sense also to break down its chemical structure. Such a concept might be invoked to explain, for instance, the effect of alkaline conditions, which are able to convert fatty acids and fatty esters to dispersible sodium salts (McBain *et al.* 1929; Mercantili *et al.* 2014). Enzymes clearly can play a similar role, since they are able to catalyze the hydrolytic breakdown of a wide range of substances that can be serving as the binders in various kinds of dirt. Several classes of enzymes are of particular interest for detergent formulations, as considered below.

Amongst the main enzymes used in detergents, proteases and lipases belong to the pancreatic enzyme family; cellulases and amylases are glycoside hydrolases (Olsen and Falholt 1998). Most enzymes today are produced by aerobic batch or continuous fermentation, on sterilized nutrients. They are based on such feedstocks as corn starch, sugars, or soy grits with the addition of salts. The enzymes are harvested after the filtering out (or centrifuging) of insoluble products and the produced biomass. Afterwards, enzyme in solution is concentrated through evaporation, membrane processes, and crystallization. After post-treatment, formulations are manufactured; the detergents are prepared either in powder form, as a nondusting granulated enzyme, or as liquid detergents, in liquid or encapsulated form (Olsen and Falholt 1998).

Enzymes are seen as an environmentally-friendly component in detergents not only because they are derived from renewable resources, but also because of their washing time, energy, and water consumption savings due to equivalent performance at lower temperatures, as well as the resulting contributions in "greener" wash-water effluents and lower pH in wash liquor and fabric care (Olsen and Falholt 1998).

Lipases

Fats associated with human skin are often a prominent component of the soiling of clothing (Sonesson *et al.* 2007; Do *et al.* 2015). As illustrated in Fig. 15, lipases have evolved to cleave such fats into their component fatty acids and glycerol (Sharma *et al.* 2001). Lipases added to detergent formulations have been shown to be effective (Fujii *et al.* 1986; Aaslyng *et al.* 1990; Sonesson *et al.* 2007). For example, Fujii *et al.* 1986) showed that lipase was effective for the removal of olive oil from cotton fabric. Aaslyng *et al.* (1990) showed that the lipase treatment was much more effective under alkaline pH conditions, which is consistent with the conversion of the fatty acids to their more hydrophilic carboxylate form.

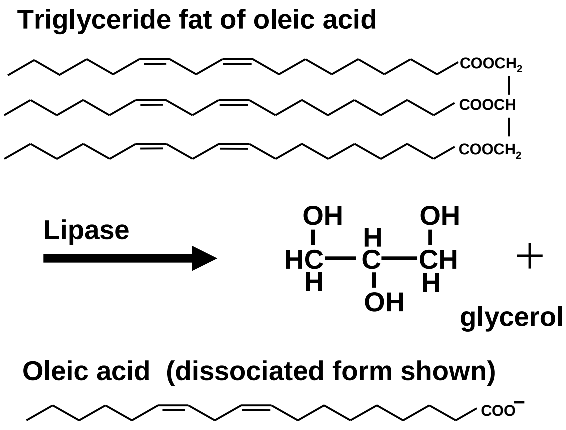

Fig. 15. Role of the lipase enzyme in hydrolysis of triglyceride fats. The reagent (triglyceride fat) in the presence of lipase reacts to form glycerol and oleic acid.

Lipases work by hydrolyzing hydrophobic triglycerides into more hydrophilic mono- and diglycerides, free fatty acids, and glycerol, which are all soluble in alkaline conditions. Interestingly, the optimal activity of lipases was found to be at 20 to 40% moisture concentration on a fabric during line-drying at room temperature. This finding helped explain the delay in cleaning efficacy, whereby the effectiveness of lipase appeared to increase after several washes (Olsen and Falholt 1998).

By breaking down lipid-based stains, lipases can also act as alternatives to surfactants in detergent formulations that are trying to decrease chemical ingredients and increase biobased content (Dybdahl Hede 2020).

Amylases

Starch can be present in a variety of soil types, such as soiling due to foods. The term amylase covers a variety of enzymes, including some of them that are effective in breaking down amylopectins and starch derivatives (van der Maarel *et al.* 2002). As shown by Tanaka and Hoshino (1999), amylase addition to a detergent formulation can enhance the results of laundering. Such treatment can be valuable if there are food stains.

The preferred amylases in detergent use are α-amylases, as they catalyze the endo-hydrolysis of starch, with excellent performance in lower temperatures and milder chemical detergent formulations. In contrast, β-amylases catalyze exo-hydrolysis of 1,4-α-D-glycosidic linkages, which is not as efficient in terms of stain removal and is therefore not used in detergents (Aehle 2007).

In addition to working to slowly degrade starch via swelling and gelatinization, α-amylases also prevent the swollen starch from adhering to the textile surface. During the enzymatic breakdown, α-1,4-linkages in starch are hydrolyzed, resulting in a conversion to water-soluble dextrins and oligosaccharides (Olsen and Falholt 1998).

One challenge for starch stain laundering has been that the gelatinized starch can form a thin coating layer on the surface of the textile, which can contribute to the increase of particulate soil pick-up, resulting in greying of white-colored fabrics after multiple washes. This film-forming will depend on the amylose content of the particular starch and can make it more difficult to remove the starch stain and particulate soiling combination. However, amylases have been shown to contribute to whiteness and prevention of graying caused by the combination of starches and particulate soiling in laundered fabrics (Olsen and Falholt 1998).

Proteases

Proteins are often present in soiled garments due to the rubbing against human skin during usage. For instance, sebum is a protein-based soil substance that can accumulate in clothing (Murata *et al.* 1991). Aaslyng *et al.* (1990) determined the aqueous conditions (*e.g.* pH and temperature) needed to achieve effective results with selected proteases when used as components in detergents. It was proposed that the proteases converted the original proteins to smaller and more water-soluble fragments. Florescu *et al.* (2009) reported that protease improved the removal of food stains during laundering in the presence of anionic surfactants.

Proteases are the most widely used enzymes in detergents and they are known as the main enzymes to contribute to environmental savings by helping reduce washing times, temperature, and water consumption. They are usually classified based on their origin (plant, animal, or microbial), their catalytic actions (endopeptidase or exopeptidase), and type of active site. Four different protease families are recognized based on comparison of active site, catalytic residue, and 3D structures: serine, thiol, aspartic, and metalloproteases. Serine proteases are further sub-divided into chymotrypsin-like and into, what is most commonly used in detergents, subtilisin-like proteases (Olsen and Falholt 1998).

Proteases used in commercial detergents are mostly similar in structure, with variation in pH and temperature optimum, bleach sensitivity, and calcium ion demand. Protease performance is influenced by detergent pH and ionic strength, as well as by type of surfactant used, which can also have an impact on its stability in the wash. Also, while proteases need a small amount of calcium in the detergent to maintain their stability, their performance generally decreases with increasing calcium concentration; accordingly, accurate proportions are key (Aehle 2007).

One of the main challenges for proteases used in liquid detergents is their instability in aqueous environments. This challenge is currently addressed by the use of inhibitors, which help prevent activity and autodigestion, as well as potential degradation of other enzymes. Some examples of inhibitors used to stabilize proteases in liquid detergents are polyols in combination with boric acid, amino acids, and protein hydrolysate products. These are all diluted during the wash (Olsen and Falholt 1998).

On the other hand, in powder detergent formulations containing bleach, storage stability can be a potential issue, as the amino acid methionine in the protease molecule can be oxidized by the bleach, leading to the deactivation of the protease enzyme. In newer protease systems, this is addressed by the replacement of methionine in the position closest to active site, with other amino acids that are insensitive to oxidation (Aehle 2007).

Cellulases

Cellulose-degrading enzymes have been widely studied for usage in detergent formulations that are specifically intended for laundering of cotton and other cellulose-based textiles (Obendorf 2004). It is important to balance the effectiveness of such systems for detergency with concerns about excessive hydrolytic breakdown of the fibers. Sufficiently high dosages and durations of treatment will convert the material to monomeric sugars (Eriksson *et al.* 2002). Nevertheless, cellulases have been introduced as a component in detergent products (Aaslyng *et al.* 1990).

Hoshino *et al.* (2000) showed that cellulase by itself was able to achieve equivalent results to treatment with surfactants and builders. The cited authors stated that enzymatic hydrolysis mainly affected the amorphous regions of cellulose. It was proposed that the effectiveness of the treatment was attributable to the lodging of dirt in those same amorphous cellulose regions. In contrast, de Souza Moreira *et al.* (2016) and Olsen and Falholt (1998) both argued that cellulase targets the crystalline part of cellulose. According to Olsen and Falholt (1998), the cellulase molecule is often composed of up to three functionally unique domains: the core, a linker, and a cellulose-binding domain (CBD). They also mention that CBD is responsible for binding on insoluble and crystalline cellulose for hydrolysis. Similarly, de Souza Moreira *et al.* (2016) also highlight CBD as the necessary accessory in the breakdown of crystalline cellulose structure (Olsen and Falholt 1998; de Souza Moreira *et al.* 2016).

Murata *et al.* (1991, 1993) found that cellulase in a detergent formulation was effective for the removal of sebum from cotton clothing. Figure 16 indicates the three main classes of cellulase enzyme, which respectively cleave randomly, adjacent to the chain ends, and breakup of cellobiose or cellotriose.

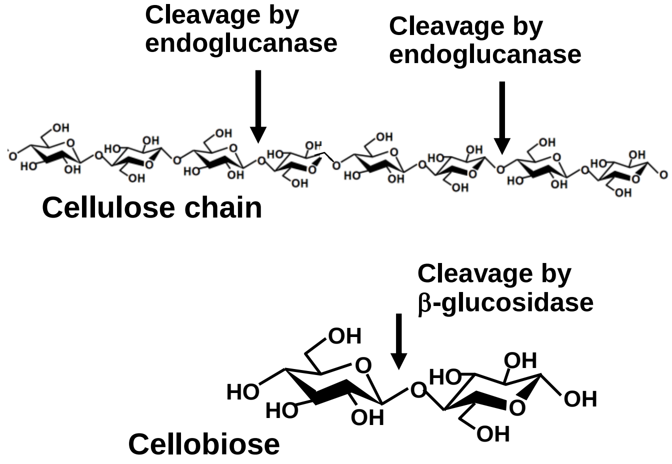

Fig. 16. Sites of hydrolytic cleavage be three categories of the cellulase enzyme

In solid phase, endo-glucanases and exo-glucanases (cellobiohydrolases) carry out the primary hydrolysis of cellulose, while β-glucosidases are responsible for secondary hydrolysis in the liquid phase. Cellulases are usually a mixture of endo-glucanases, cellobiohydrolases, and β-glucosidases. Endo-glucanases and cellobiohydrolases tend to only attack the external cellulose chains, without diffusing inside the fibers, which is important when considering the potential extent of degradation of the cellulosic fiber during washing (de Souza Moreira *et al.* 2016). This translates into the elimination of pilling and fuzz from the surface of the cellulosic fabric during washing, which is a feature specific only to the cellulase enzyme (Olsen and Falholt 1998).

In addition to cleaning the textile through the hydrolysis of glycosidic bonds, cellulases provide the additional benefit of softening and brightening the color of the used cellulosic fabric, hence the name “color clarification cellulase” (Olsen and Falholt 1998).

From a process standpoint, it is important to keep in mind optimal conditions of cellulase use when incorporating in a detergent, due to the concern that temperatures higher than 80 °C might deactivate the enzyme (Rahman *et al.* 2021).

Mannanases

Although not as widely-used as pectinases, mannanases are enzymes also used to target hard-to-remove stains containing mannanolytic compounds, of such products as gravy, ice cream, ketchup, and mayonnaise, amongst many. Mannan endo-mannosidase degrades the β-1,4-mannose linkage of galactomannans, which is found in neutral pectin-containing food products, as well as in cosmetics, household products, and toiletries. Mannan, the gum polymer, is then broken down into a smaller molecule, making it more water-soluble, so it can be easily removed during laundering. Aside from being an effective stain removal agent, mannanases are also knows to help prevent redeposition of soil (Aehle 2007; David *et al.* 2018; Dybdahl Hede 2020).

Multi-enzyme systems

While above sections describe distinctive functions of individual enzymes, multi-enzyme systems have become more widely used for several reasons. Firstly, many detergents use multiple enzymes in order to increase the enzyme tolerance for other ingredients, such as surfactants, builders, and bleaching agents. Second, as detergents are more and more often formulated for use in colder temperatures, use of multi-enzyme systems increases their efficiency, especially with regards to starch and fat soiling. Lastly, when looking at increasing environmental savings, they allow for elimination of phosphates without much impact to detergent’s cleaning performance (Dybdahl Hede 2020).

The use of multiple enzymes in a detergent recipe is not new. Between 1967 and 1970, combining amylases, cellulases, and lipases resulted in first advances in energy savings in textile laundering (Olsen and Falholt 1998). Some examples of performance enhancement with regards to stain removal by multiple enzyme formulations includes the common use of amylases and pullulanases to achieve a more complete degradation of starch. Additionally, bacterial α-amylases remain stable in presence of proteases in both, powder and liquid formulations, during storage (Aehle 2007).

Stabilization of enzymes

Some studies have found synergistic effects between surfactants and enzymes (Traore and Buschle-Diller 1999; Iyer and Ananthanarayan 2008; Seo *et al.* 2011). In the case of cellulase, increased hydrolysis sometimes has been attributed to an ability of the surfactant to mitigate the unproductive binding of the enzymes to lignin, which has a more hydrophobic character than cellulose (Zeng *et al.* 2014). Ooshima *et al.* (1986) attributed faster hydrolysis of cellulose to the ability of a surfactant to hold the cellulase in the liquid phase. Lou *et al.* (2018) showed that nonionic surfactants were able to partly protect cellulase from deactivation in the presence of hydrodynamic shear.

Future opportunities in detergent enzymes research

Recently, a new variety of enzymes, called extremozymes, has appeared as a potential enhancement to current enzyme use in laundry detergents. Extremozymes are essentially optimized enzymes, capable of remaining active and stable under extreme conditions. They are mainly engineered for use in cold water temperatures and in alkaline pH, and are said to be on track to eventually replace the mesophilic enzymes due to their higher efficiency. Currently, some examples of extremozymes available for detergents are cold-active proteases, lipases, cellulases, amylases, pectate lyases, and type I pullulanases; alkaline proteases and lipases; thermophilic and alkalophilic mannanases; thermostable pectinases; thermo-alkaline cutinases; and alkaliphilic xylanases. However, the specific nutrient requirements, environmental factors, and maintenance of the strains is still an issue. Additionally, as extremozymes have low thermal stability and lesser shelf life, more research is needed to allow for their commercial use in detergent products (Al-Ghanayem *et al.* 2022).

Another process improvement sought after in enzyme use optimization for detergents is the implementation of smart enzyme delivery systems. Such dosing systems would allow the automatic release of the active ingredient only at the stage of washing when it is specifically needed. Such improvement would build on enzymes' compactness and suitability for concentrated detergent formulations. This would in turn allow for reduced chemical use, cost savings, as well as reduced water and energy consumption, all while optimizing cleaning performance (Olsen and Falholt 1998).

Finally, Aehle (2007) listed a plethora of innovative enzymes being worked on for detergent applications, such as low-allergenicity enzymes, redox enzymes, targeting enzymes, as well as enzymes of psychrophilic and extremophilic organism origin. Redox enzymes, such as peroxidases, haloperoxidases, and laccases, have the potential to offer cost-savings and utilization of less-harmful chemicals thanks to their ability to deliver parallel bleaching performance at lower washing temperatures. Advances in protein engineering, genomics, and proteomics will ultimately drive these new developments in detergent enzyme components.

Bleach Components

Bleaching agents are commonly used in laundering (Matheson 1996; Upadek *et al.* 1996; Bianchetti *et al.* 2015). Often the bleaches are added separately, thus allowing the user to make decisions related to the tolerance of different items of clothing to bleaching. In principle, bleaching agents can contribute to laundering in two ways. First, by decolorizing various chromophoric groups, the bleach makes the material seem less soiled (Oakes 2005). Second, many bleaches are oxidizing agents, and the products of oxidation are often more soluble in water (Moskaliuk and Katović 1997). However, as shown by Li *et al.* (2012), the addition of bleach to a detergent formulation can increase the damage to fabrics during washing. Adverse effects of bleaching in laundering on the environment also need to be considered, since chlorinated aromatic compounds can be formed and discharged to waterways (Moskaliuk and Katović 1997). To address this, researchers have been looking into the use of redox enzymes, such as peroxidases, haloperoxidases, and laccases, to help replace the traditional bleaching systems with equivalent enzyme-based bleaching performance at lower washing temperatures. Mono- and dioxygenases have also been explored as alternative bleaching agents through direct oxidation of the substrate (Aehle 2007).

New Trends in Bio-based Detergents

Surfactants have been conventionally manufactured from fossil sources that are involved in the most significant generation of global warming emissions (Hayes and Smith 2019). In this context, the replacement of petroleum-derived surfactants with bio-based components has been proposed as a means toward increasing progressively their eco-friendly character (Hayes and Smith 2019; Bettenhausen 2022; Ortiz *et al*. 2022). Besides biodegradability, the decreasing of carbon release during surfactant manufacturing process is nowadays considered as one of the most important socio-economical aspects in their production (Homma *et al.* 2008; Santos *et al.* 2016; Alwadani and Fatehi 2018; Hayes and Smith 2019; Jadhav *et al.* 2019; Ortiz *et al*. 2022). As a result, several strategies regarding renewable sources to produce bio-based surfactant and their components have arisen, which are reviewed in this section. In addition, there appears to be a popular demand for products that can be listed as "bio-based" (Bettenhausen 2022). Examples shown in the cited article include lauryl glucoside (inherently bio-based), sodium lauryl ether sulfate (semisynthetic), rhamnolipid (biosurfactant), and sophorolid (biosurfactant).

Surfactants from carbohydrate derivatives

Carbohydrates are the most abundant organic compounds worldwide and are classified as monosaccharides and polysaccharides (Santos *et al.* 2016; Hayes and Smith 2019; Ortiz *et al.* 2022). Glucose and other sugars are the most representative of the monosaccharides and can be obtained from the enzymatic hydrolysis of cellulose, the most abundant of the polysaccharides (Ortiz *et al.* 2022; Vera *et al.* 2022a,b). Glucose is likewise the most abundant monosaccharide in nature. It can serve as a raw material for manufacturing a marriage of value-added building blocks at industrial scale such as succinic acid, levulinic acid, itaconic acid, maleic acid, lactic acid, and 5-hydroxymethyl furfural (5-HMF) (Willke and Vorlop 2001; Delhomme *et al.* 2009; Saxena *et al.* 2017; Schmidt *et al.* 2017; de Carvalho *et al.* 2018; Ortiz *et al.* 2022; Vera *et al.* 2022b). In this sense, the abundance of hydroxyl groups makes monosaccharides and their chemical derivatives feasible to be the polar head of surfactant molecules. The production of these types of surfactants has a low carbon footprint and may potentially have low toxicity, biodegradability and biocompatibility for pharmaceutical, food, and detergency applications when compared to fossil-based surfactants (Hayes and Smith 2019; Jadhav *et al.* 2019; Koteich Khatib *et al.* 2020; Ortiz *et al.* 2022). Surfactants that incorporate monosaccharides as a hydrophilic group have become well known (Saleeb 1970; Fanun *et al.* 2010; Ortiz *et al.* 2022).

Ortiz *et al.* (2022) compiled a marriage of surfactants made from building blocks and chemicals derived from biomass carbohydrates. Bevinakatti and Waite (2012) synthesized, from succinic acid, a sorbitol succinate (oligo laurate) that provides well-proven interfacial properties. The reaction of succinic acid with polyglycerol and a monocarboxylic acid has been reported to form an oligomeric surfactant under acid/bases catalysis at 200 °C (Santos *et al.* 2016; Hayes and Smith 2019; Ortiz *et al.* 2022). Moreover, nonionic surfactants have been synthesized from oligoesters, in which the hydrophilic part is formed by succinic acid and glycerol units, whereas lauric acid serves as the hydrophobic part (Agach *et al.* 2016, 2018). On the other hand, several approaches to synthesize bio-based surfactant components from other carbohydrate derivatives such as succinic acid, fumaric acid, itaconic acid, furfural, and 5-HMF have been reported (Santos *et al.* 2016; Hayes and Smith 2019; Ortiz *et al.* 2022).

Surfactants from vegetable oils

The worldwide consumption of vegetable oils and fats for surfactant making is expected to increase considerably due to their inherent biodegradability and renewability (Hayes and Smith 2019; Jadhav *et al.* 2019). Vegetable oils have always been an important source for making surfactants, where saponification is the oldest production process (Hayes and Smith 2019; Jadhav *et al.* 2019). Fatty acids and triglycerides from vegetable oils can be chemically modified to provide interfacial properties for several applications, including detergency (Santos *et al.* 2016; Jadhav *et al.* 2019). Glycolipids are common biosurfactants that are made from the fermentation of vegetable oils (*e.g.*, Soybean oil, corn oil, coconut oil, sunflower oil, cottonseed oil, palm oil, and olive oil) (Santos *et al.* 2016; Hayes and Smith 2019; Jadhav *et al.* 2019). In addition, several detergents and surfactants types (*e.g.*, amphoteric, ionic, and nonionic) can be synthesized *via* amination, sulfonation, ethoxylation, epoxidation, and esterification processes applied to vegetable oils (Pratap *et al.* 2011; Hayes and Smith 2019). The properties of surfactants made of vegetable oils can change based on the nature and composition of the oil (*e.g.*, triglycerides, carbon-chain distribution, *etc*.). Coconut and palm oil are the most used vegetable oils in the production of surfactants due to their unique and large proportion of C_{12} fatty acids and low levels of unsaturation that provides high foam ability and detergency (Pratap *et al.* 2011; Santos *et al.* 2016; Hayes and Smith 2019). Others have used vegetable oil sources such as canola and soybean oil, which have a high proportion of C_{18} fatty acids with much higher levels of unsaturation that provides less hydrophilic surfactants (Pratap *et al.* 2011; Santos *et al.* 2016; Jadhav *et al.* 2019). Several extracted oils can be used for surfactant synthesis even when they can be produced in a lower ratio compared to the conventional oils (Pratap *et al.* 2011). For example, a surfactant synthesized using the oil from the cashew nut shell has been reported to have antibacterial and interfacial properties that make it promising for detergency applications (Koteich Khatib *et al.* 2020). Palm kernel, jatropha, soapnut, olive, cottonseed, and rapeseed have also been reported to be used to synthesize biosurfactants (Hayes and Smith 2019).

Lignin-derived detergents

Lignin is an abundant organic polymer that has been tagged as a potential substitute for conventional surfactants made from fossil sources (Homma *et al.* 2008; Alwadani and Fatehi 2018). This low-cost polymer is mostly obtained from pulping processes of the pulp and paper industry, where it is usually burned to generate energy (Alwadani and Fatehi 2018; Li and Takkellapati 2018). However, lignin has been reported to be a promising raw material for surfactant making even when having an undefined polymeric structure that challenges the making of defined products (Homma *et al.* 2008; Alwadani and Fatehi 2018). Soda, kraft, and lignosulfonates are the most common types of lignin, among which the lignosulfonates are highly soluble in water (Jardim *et al.* 2020). On the other hand, kraft and soda lignins lack water solubility and need an alkaline medium to be solubilized in water (Ou and Zhao 2017; Li and Takkellapati 2018; Jardim *et al*. 2020; Gong *et al*. 2022). Regarding surfactants derived from lignin, several processes such as alkylation, amination, carboxylation, acylation, halogenation, methylation, oxidation, reduction, sulfomethylation, sulfonation, and epoxidation have been developed to modify and increase the amphiphilic character of lignin (Hayes and Smith 2019; Jadhav *et al.* 2019; Ou *et al.* 2021). Thus, more hydrophilic functional groups can be added in the original lignin structure to produce promising, lignin-derived surfactants (Alwadani and Fatehi 2018). Lignin-poly(ethylene oxide) has been reported to have similar amphiphilic behavior compared to conventional nonyl-phenol, non-ionic surfactants (Homma *et al.* 2008; Alwadani and Fatehi 2018; Ou *et al.* 2021). Moreover, the modification of lignin with polyethylene glycol di-glycidyl ethers has been reported to generate modified lignin with interfacial properties able to decrease the water surface tension from 72.8 to 28 mN/m. Hence, those amphiphilic lignin-based surfactants have potential applications as detergents and emulsifiers for oil-in-water emulsions (Alwadani and Fatehi 2018). Other studies report that lignin modified via alkylation, sulfonation, and oxidation produces high quality surfactants able to reduce water surface tension down to 0.32 mN/m (Homma *et al.* 2008; Alwadani and Fatehi 2018; Ou *et al.* 2021).

Potential challenges in the use of lignin-derived detergents are the inconsistency in purity and limited efficiency, as well as processing difficulty due to their complex structure, unreactive nature and differences amongst the different lignin types and pulping processes used. As a result, lignin-based surfactants that are surface-active in different systems could offer a viable component for detergent products in the future (Alwadani and Fatehi 2018).

Another challenge is that functional groups in lignin-derived products may be protonated/deprotonated at different pH, causing variance in surface activities. To address this variance, pK and solubility should be considered at the time of lignin derivative selection (Alwadani and Fatehi 2018). Similarly, it is worth noting the electrostatic interactions between certain enzymes and lignin. At high pH, enzymes and lignin become negatively charged, which reduces their affinity. Additionally, the presence of surfactants in detergents further reduces that affinity through its impact on hydrophobic effects, as well as through formation of hydrogen bonds with lignin. In their study, Fritz *et al.* (2015) found that electrostatic interactions between cellulase and native lignin resulted in ~20% reduction in enzyme affinity at pH 5.5.

Modified lignosulfonates as detergent builders

In principle, by replacing various petroleum-derived components of surfactants with bio-based components there is potential to progressively increase their eco-friendly character. Ou and Zhao (2017) modified lignosulfonate with polypropylene glycol and found that the product was effective as a detergent builder. Due to its composition, one might also classify this product as a surfactant.

Lignosulfonates are also inexpensive materials and, in comparison with kraft lignin, possess a hydrophilic sulfonate group attached to a hydrophobic and aromatic chain (Ou and Zhao 2017; Alwadani and Fatehi 2018; Gong *et al*. 2022). This characteristic of lignosulfonates makes them suitable to be used as natural surfactants, dispersants, and flocculants (Homma *et al.* 2008; Xu and Ferdosian 2017; Alwadani and Fatehi 2018; Ou *et al.* 2021). Sulfonate's negative charge, in combination with the inherent hydrophobicity of the aromatic groups, means that lignosulfonates are capable of being adsorbed on surfaces, which promotes both surface charge and wettability changes (Ou and Zhao 2017; Gong *et al.* 2022). However, they do not have a significant effect on reducing interfacial/surface tension, which is an important limitation in their applications (Alwadani and Fatehi 2018; Homma *et al*. 2008; Ou *et al*. 2021). Thus, as well as kraft lignin, chemical modification such as sulfonation, oxidation, carboxylation, and epoxidation processes are reported to improve significantly the surfactant performance of lignosulfonates (Ou and Zhao 2017; Gong *et al*. 2022). Regarding detergency applications, Ou and Zhao (2017) modified lignosulfonate with polypropylene glycol and found that the product was effective as a detergent builder. When compared to commercial dodecyl benzene sodium sulfonate, modified lignosulfonate had 10% higher detergency. On the other hand, lignosulfonate has been reported to significantly improve the prevention of ash deposits on cotton fibers during the laundry process (Gong *et al.* 2022). Additionally, lignosulfonates can act as chelating agents to remove Ca^{2+} and Mg^{2+} from hard water and improve the detergency effect of the main surfactant laundry formulation (Ou and Zhao 2017; Xu and Ferdosian 2017).

Characteristics of the Dirt

The word “dirt” is often used in the field of detergency to denote the contaminant material that is being removed during a washing or laundering process. One of the challenges in understanding detergency is the fact that the character of the dirt is not always the same. To make sense of this, dirt has been categorized based on various criteria, as follows.

Wettability

The degree to which a substance is wettable by water can be assessed by placing a small water droplet on a flat surface and measuring the angle of contact, which is drawn through the water phase (Berg 1993; Hubbe *et al.* 2015). The geometry is shown in Fig. 17. As indicated in the figure, contact angles also can be determined based on the profiles of droplets on single filaments of a textile (Carroll 1976, 1993).

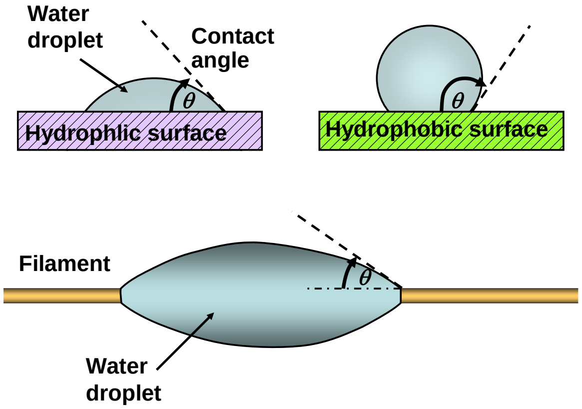

Fig. 17. Contact angles of a water droplet onto flat hydrophilic *vs.* hydrophobic surfaces, where a surface with a contact angle < 90° is “wettable”, and a surface with a contact angle < 90° is nonwettable. Also: definition of contact angle when evaluating droplets symmetrically attached to single filaments

The contact angle is important, in principle, since it determines the tendency for a liquid to advance across the surface of another material (Carroll 1993), which is a requirement for any washing process. Banerjee *et al.* (2012a) recommended complete wettability (essentially a contact angle of zero) as a criterion for effective washing. According to Sanders and Lambert (1950), one of the most traditional forms of simulated dirt, for the purposes of assessing detergent formulation, is a hydrophobic mixture of carbon black and fat. As will be discussed later, different mechanisms of soil removal appear to be dominant depending on whether the solid materials, including the dirt, are hydrophilic or hydrophobic (Chanwattanakit and Chavadej 2018). According to Chanwattanakit *et al.* (2019), the effectiveness of detergency is often highly correlated to the contact angle of a detergent solution on the surfaces being considered. Phaodee *et al.*

(2019) reported a similar relationship in the case of detergents designed for cold water use. A particularly challenging type of dirt to remove from textiles is used motor oil (Chi and Obendorf 1999). Not only is the oil highly hydrophobic (giving a large contact angle with water), but it also contains effective dispersants, allowing it to penetrate readily into the material that needs washing.

Melting or softening point

As will be seen later in this article, whether the dirt can be described as liquid or solid can make a difference in terms of the detergency mechanisms and the strategies that are likely to be effective. Such issues are essentially about the melting point or the softening point of a continuous phase within the dirt (Chanwattanakit *et al.* 2017; Chanwattanakit and Chavadej 2018). Some common components of dirt present on soiled fabric will tend to be more solid-like under conditions of cold-water washing (Phaodee *et al.* 2019).

Stains

Stains can be defined as persistent, undesired colorants (Kert and Simoncić 2008; Ponnusamy *et al.* 2008; Pukale *et al.* 2017; Bueno *et al.* 2019). Many of them are organic compounds having strong ability to absorb light (Luxbacher *et al.* 2008). Some of them can be broken down by use of enzymes (Aaslyng *et al.* 1990; Tanaka and Hoshino 1999; Florescu *et al.* 2009). Rojvoranun *et al.* (2012a) used that criterion that staining would involve some kind of chemical bonding with the substrate, though such a definition does not appear to be widely applied in the literature.

Triglyceride fats

Fats can come both from the skin and from foods (Fujii *et al.* 1986; Miller and Raney 1993; Miñana-Perez *et al.* 1995; Obendorf 2004). Though the triglyceride fats themselves are quite hydrophobic, the action of natural lipase enzymes often converts them in part to the component fatty acids or the associated calcium salts (Fujii *et al.* 1986). Thus, the related dirt on textiles is likely to be a mixture.

Equivalent alkane carbon numbers for oily phases

When comparing the effects of different oily materials, researchers have found it advantageous to categorize compounds in terms of their equivalent alkane carbon numbers (EACN) (Phaodee *et al.* 2020; Chen *et al.* 2022). Thus, the presence of a carbon-carbon double bond within a linear alkyl chain often leads to properties equivalent to those of a saturated chain with two less carbons in it (Brito *et al.* 2011; Hubbe *et al.* 2020). The difference has been attributed to the poorer packing ability of the unsaturated alkyl chains.

Susceptibility to degradation

The susceptibility to being broken down by moderate aqueous conditions or enzymes can provide a pathway for strategies in detergency. For example, simple esters, as well as simple protonated carboxylic acids, can be converted to more soluble sodium salts by alkaline solutions of suitable strength and temperature (Sharma *et al.* 2001). The same ester bonds, as well as the amide bonds within proteins (Murata *et al.* 1993; Obendorf 2004) are also susceptible to enzymatic breakdown.

Adhesion of dirt

Given the diverse nature of dirt, one can expect that different adhesion factors will be important in different cases. The adhesion of solid particulates, under dry conditions, may involve relatively straightforward van der Waals forces, in particular the London dispersion component (Hubbe 1984; Visser 1995). Triboelectric effects can be involved, especially as a mechanism by which dust particles can be gathered into the surfaces of contrasting material surfaces in the presence of rubbing (Matsusaka *et al.* 2010). In addition, the capillary condensation of water at tiny interfacial zones can have a significant effect, especially for very small particles and at high levels of relative humidity (Fisher and Isrealachvili 1979; Bocquet *et al.* 1998).

When dirt is in liquid form, or when it has passed through a liquid phase while present on a fabric surface, it is likely that wetting of the substrate surface by the dirt droplet will have occurred. When the wetting involves water, the hydrogen bonds that develop between the solids during drying can substantially contribute to adhesion (Hubbe 2006; Gardner and Tajvidi 2016); however, in such cases that component of adhesion usually can be reversed by rewetting of the material. What can be more of a challenge is when a liquid, non-polar phase spreads on a textile surface, often serving as a binder for other dirt components. Such situations may be dominated by the less strong van der Waals forces. However, if the wetting is favorable, the molecular contact may be intimate and complete. Such systems can represent the main challenge for which detergent systems are designed, especially when the dirt becomes spread within the fibrillar or pore structure of fabrics (Murata *et al.* 1991; Chi and Obendorf 1999; Obendorf 2000). Enzyme systems can be effective against challenging colorants including blood and chocolate (Paul *et al.* 2014).

Laundering Technologies

Before considering the mechanisms of detergency, it is important to summarize some basic features of conventional laundering procedures. Most household laundering is carried out in equipment such as those shown in Fig. 18. The widely-used top-loading version, as shown in Part A of the figure, requires the usage of a specialized agitator to impart effective motion of fabric and of detergent solution. By contrast, the turning of the drum of a front-loading washer is expected to impart a repeated tumbling effect, so no agitator is used.

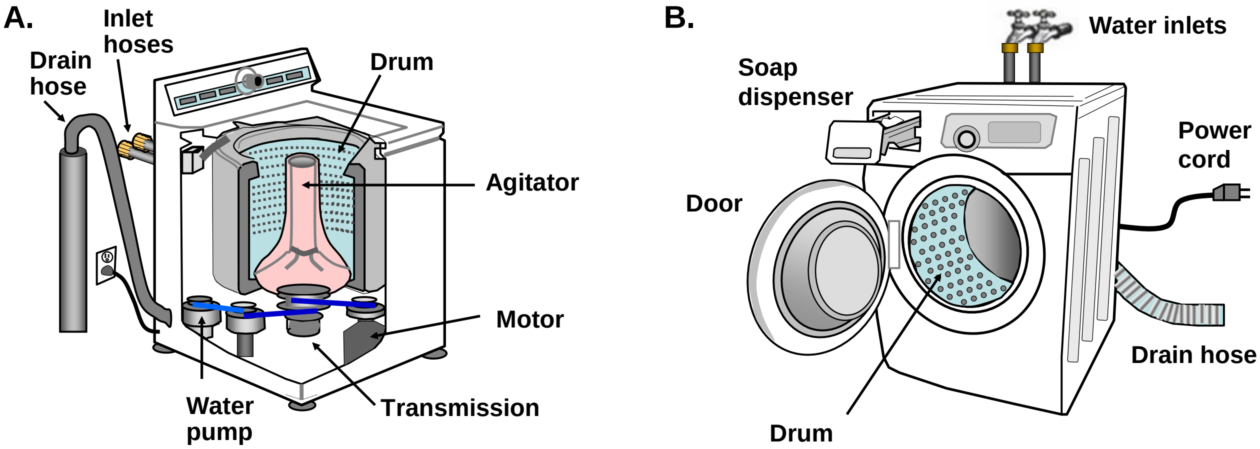

Fig. 18. Schematic views of two major formats of home washing machines: A: Top-loading; B: Front-loading

Many academic studies of laundering have employed simplified equipment. For instance, Bubl (1970) provides a useful baseline by describing a six-university study involving the laundering of cotton garments. Strictly nonionic surfactants were used, which is a simplification over the presently more commonly used formulations that include anionic and extended surfactants. Briefly stated, laundering involves agitation of cloth items in the presence of a variety of detergent components, as outlined in earlier subsections. A variety of flow patterns cause the aqueous solution to flow both past the cloth surfaces and through the laundered items. The washing stage is followed by rinsing stages, which include spin cycles (centrifugation) to remove water, in addition to dilution cycles in which fresh water is added. Figure 19 illustrates four types of mechanical action that have been mentioned in articles related to detergent action.

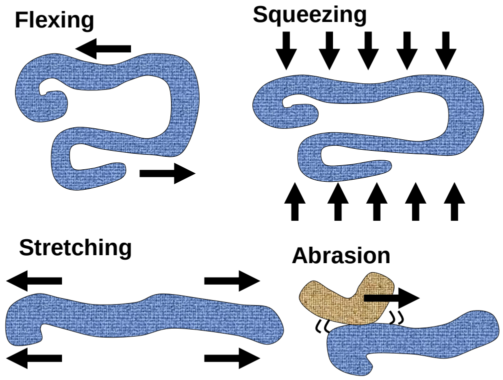

Fig. 19. Examples of mechanical actions imparted to textile items during laundering

Hydrodynamic shear

Several researchers have set out to find how flow conditions affect the outcome of conventional laundering. In particular, Lee *et al.* (2008) studied the effect of flow action, fabric flexing, and abrasive rubbing on laundering outcomes. Of these, abrasion was found to have the biggest effect. Yun *et al.* (2017) likewise reported that a rubbing action was the most effective in removal of dirt, compared to other regimes studied. Muir *et al.* (2013) reported that flow through the fabric had a greater beneficial effect on the results compared to cross-flow or combined-flow regimes. van der Donck (1997), on the contrary, proposed that a squeezing effect was especially important in dislodging dirt. The cited author felt that conventional washing machines tended not to provide sufficient squeezing motions. Follow-up work (van der Donck 1999) showed that dirt removal increased with increasing flow rate, up to a plateau, and then it did not increase further. Pulsating flow was found to be more effective than other flow regimes. Stretching of the fabric, as a result of hydrodynamic forces, also seemed to be effective in releasing dirt. Yun *et al.* (2013) and Yun and Park (2015a,b) likewise reported that complex motions of fabric were associated with the highest efficiency of dirt removal during laundering. Akcabay *et al.* (2014) carried out simulation work to quantify various flows and shear stresses during conventional laundering. Various studies have confirmed the critical importance of hydrodynamic action, working together with detergent components, in bringing about effective washing (Li and Hardin 1998; Caparrós *et al.* 2012; Muir *et al.* 2013; Han *et al.* 2015; Bueno *et al.* 2019). Notably, hydrodynamic shear can be expected to provide the energy input that is required by such detachment mechanisms as roll-up and snap-off (Dillan *et al.* 1979; Miller and Raney 1993).

Temperature

According to classical studies, detergency has been found to become more effective with increasing temperature (Bubl 1970; Kaewpukpa *et al.* 2008; Muir *et al.* 2013; Chanwattanakit *et al.* 2017). This can be attributed partly to a softening of some types of dirt (Chanwattanakit *et al.* 2017). In addition, higher temperatures tend to accelerate a wide range of reactions, including saponification and enzymatic hydrolysis (Komaki *et al.* 2002). Especially in recent decades, there has been a push for effectiveness of detergent systems at lower temperatures, and many commercially available detergents are specifically designed for those conditions (Benson *et al.* 1985; Azemar *et al.* 1993; Do *et al.* 2015; Attaphong and Sabatini 2017; Phaodee *et al.* 2019).

Time

Detergent action takes time. Several articles have considered the duration of exposure to detergent solution needed to achieve suitable washing results (Dillan *et al.* 1980; Fujii *et al.* 1986; Burkinshaw and Anthoulias 1996; Herrera 1996; Hoshino *et al.* 2000; Komaki *et al.* 2002; Kaewpukpa *et al.* 2008; Yun and Park 2015b; Pukale *et al.* 2017; Bueno *et al.* 2019; Isaka *et al.* 2021). It is well known that processes such as enzymatic hydrolysis take time to reach sufficient completion to reach desired goals (Hoshino *et al.* 2000). Time is also required for the swelling of cellulose-based materials upon wetting (Tucker *et al.* 2010). Multiple processes are likely to require time, and it is often difficult to know which of them have important effects on the overall time required for effective washing.

Mechanical forces

In addition to flow, there is evidence that mechanical forces acting on fabric during laundering can be important (Lee *et al.* 2008; Yun *et al.* 2017). Yun *et al.* (2017) carried out tests to simulate the effects of a traditional washboard. A rubbing action was found to be effective. High washing efficiency with minimum fabric damage was found with use of a laundry bat procedure, in which the wet laundry was struck with a wide stick. Sliding, falling, and rotation motions in a washing machine appeared to have combined effects (Yun and Park 2015a). These effects were found to depend on the position of the fabric within a washing machine, which affects the speed difference between the fabric and the drum (Yun and Park 2015b). Complex movements appeared to be the most effective (Yun *et al.* 2013; Yun and Park 2015b). Carroll (1993) theorized that an imbalance of mechanical forces on a dirt particle can play a critical role in dirt release.

Ultrasonic treatment

Ultrasonic vibrations within a laundering system have been shown to promote detergent action (Warmoeskerken *et al.* 2002; Gotoh *et al.* 2015; Peila *et al.* 2015). By contrast, Gotoh (2010) observed no benefit of ultrasonic cleaning, in comparison to conventional agitation, in the case of artificially soiled clothes. The fact that not all dirt responds in the same way to ultrasonic vibrations is likely due to differences in adhesion mechanisms. On the one hand, if the attachment can be described as “brittle,” then it makes sense that localized shock waves might bring about detachment (Wang *et al.* 2018). On the other hand, the same shock waves may have low effects if adhesion is dominated by ductile interactions (Pei and Ferreira 1998).

Detergent systems

A detergent system can be defined as a multi-component mixture that usually contains at least one surfactant, an alkaline agent such as sodium carbonate, a builder such as zeolite, and a salt such as sodium sulfate, and various other components (Matheson 1996). Consumer demand for a compact surfactant required substantial reformulation (Leal *et al.* 1996). Some of the most effective detergent systems contain two or more surfactants (Tongcumpou *et al.* 2003). Though it is commonly understood that detergents are supposed to be removed from fabric during rinsing, such removal may not be complete. In particular, cold-water washing has been found to increase the amount of residual detergent components remaining in clothing (Kiriyama 2003).

Solution pH

The electrolyte conditions of the aqueous phase can play a large role in detergency. In particular, the salinity and the pH are often shifted based on the components of detergent formulations. As noted by Matheson (1996), adjustment of the pH is a major approach used in industrial laundering. Enzyme performance, for example, is often greatly influenced by detergent pH, such as with lipases, whose rate of dirt removal improves at alkaline pH (Aaslyng *et al.* 1990; Aehle 2007). With increase in pH, the solid surfaces tend to become more negative in ionic charge, due largely to the dissociation of carboxylic acid groups (Grancarić *et al.* 1997; Rojvoranun *et al.* 2012b). In addition, the penetration of water into the fabric tends to be faster at higher pH (Takahashi *et al.* 2007).

Dry cleaning

Dry cleaning employs non-aqueous solvents. In particular, perchloroethylene (PERC) has been used in dry cleaning (Lohman 2002). Although the nonpolar medium can be useful for solubilizing and removing various nonpolar soils, the effectiveness of typical dry cleaning systems is enhanced by the use of surfactants (Grunewal 1970; van Roosmalen *et al.* 2003; Soljacić and Pusić 2010). Soljacić and Pusić (2010) reported that the surfactants also helped to reduce adverse effects of static electricity during dry cleaning. However, the harmful environmental effects of PERC release from dry cleaning establishments (Lohman 2002; Ceballos *et al.* 2021) have prompted a search for alternative systems. One of the most promising alternatives to conventional dry cleaning involves the use of pressurized carbon dioxide. Under certain conditions of pressure and temperature, a carbon dioxide mixture becomes supercritical, and such systems can be effective for laundering (van Roosmalen *et al.* 2003). Figure 20 shows the regions of pressure and temperature in which carbon dioxide is in supercritical form (Budisa and Schulze-Makuch 2014). A pressure above *ca.* 74 atmospheres and temperature above *ca.* 30 °C are required.

As noted by Bannerjee *et al.* (2012a,b), cleaning with the use of supercritical carbon dioxide is greatly enhanced by the use of an optimized addition of detergent components. As explained in the cited article, the van der Waals interactions in a CO_2 system play a more dominant role in comparison to both water and PERC, which is the most common traditional dry-cleaning solvent. The surfactants help in the removal of hydrophobic compounds. Preventing the redepositing of soils at the end of the cycle has been found to be a greater challenge when using CO_2 systems (Sutanto *et al.* 2013). The cited authors reported favorable results when using either cellulose acetate or carboxymethylcellulose (CMC), as an antiredeposition aid. Banerjee *et al.* (2012b) found good results with use of a surfactant formulation that contained a branched polyoxyethyene nonionic surfactant together with n-hexane and water. van Roosmalen *et al.* (2003, 2004) reported promising results with three different surfactants in combination with supercritical CO_2. However, there was an adverse effect on detergency when the surfactants were used in the presence of isopropanol as a co-solvent. Sutanto *et al.* (2014) reported no significant improvement in supercritical CO_2 dry cleaning results when applying various types of agitation or ultrasound in addition to surfactant addition.

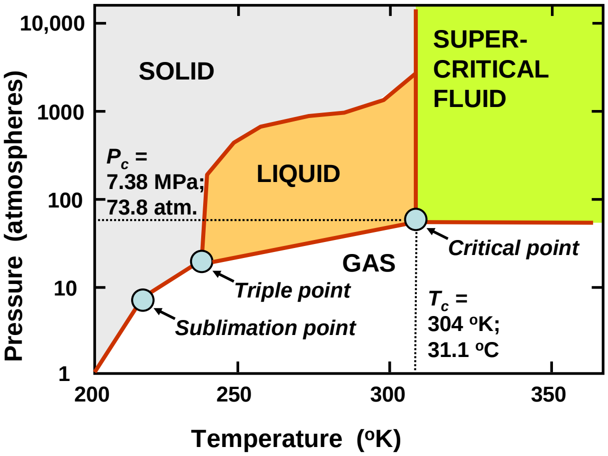

Fig. 20. Phase diagram, showing the state of matter of carbon dioxide, depending on the pressure and temperature

Wet cleaning

The term wet cleaning refers to a laundering approach that aims to have effects similar to those of dry cleaning, but without the avoidance of water (Sinsheimer *et al.* 2002; Pučić 2008; Rijavec *et al.* 2015). Soljacić and Pusić (2004) described the medium as being based on mild acid or neutral water. The solvent system also can include ethyl-hydro-oxides using ethanol, hydrogen peroxide, potassium hydroxide, and water (Jain 2017). Increasing peroxide and KOH concentrations were found to increase the cleaning of biodiesel from cotton cloth.

Table 2. Testing Methods for Detergency Evaluation

Description of Method	Citation
Light reflectance after standard soiling and washing procedure	Sanders & Lambert 1950
Gravimetric assessment of removal of fatty acids from cotton	Powe 1963
Immersion and sorption methods to assess wettability	Kissa 1981
Video microscopy	Raney *et al.* 1987
FTIR spectrometry	Scheuing & Hsieh 1988
Set-up for miniature washing machines for lab evaluations	Cahn & Feighner 1996
Microscopy, emphasizing inter-fiber spaces	Obendorf 2004
Confocal microscopy of detergent action on single fibers	Sonesson *et al.* 2007
Streaming potential tests to determine zeta potential effects	Luxbacher *et al.* 2008
Fluorescence microscopy	Ren *et al.* 2012
Conventional laundering with stain monitors and stain strips	Kruschwitz *et al.* 2013
Time-dependent color analysis	Muir *et al.* 2013
Surfactant parameter	Zarate-Muñoz *et al.* 2016
Infra-red analysis to determine detergency effects	Isaka *et al.* 2021

Testing methods

Various testing protocols have been developed to assess detergency performance. Table 2 lists some of these. It is clear that diverse methods are available to compare detergent systems and to address some mechanistic questions.

Wastewater from Detergent Usage

After completion of a household laundry cycle, the contaminated water is sent down the drain to a wastewater treatment facility (Gooijer and Stamminger 2016). Even when this is not under the direct control of the user of a detergent process, it is worth considering the likely impacts on the environment and steps that can be taken to minimize such impacts (Tripathi *et al.* 2013). According to Pusić *et al.* (2006), the conventional powder and liquid detergents that were evaluated met all of the national requirements of Croatia and Slovenia regarding wastewater. Lint that has been removed from textiles during laundering will be present in wastewater (Higgins *et al.* 2003). It is important to effectively clarify the wastewater so that this material ends up in the sludge rather than being allowed to enter streams and be carried to the ocean. Once in the ocean, the plastic components of such lint will contribute to problems associated with microplastics (Auta *et al.* 2017).

It is technically possible to recover surfactants from wastewater by the use of membrane filtration (Ciabatti *et al.* 2009). As reported by Giagnorio *et al.* (2017), the first recommended step is to carry out a pre-filtration to remove large contaminants. Subsequent use of an ultrafiltration membrane was found to be able to recover 43% to 39% of the surfactant from the detergent system, using a cut-off pore size of about 6 kDa. It was not clear, however, the extent to which the recovered surfactant still contained dirt components and oil that had been removed from the laundered items. In particular, it seems likely that anionic surfactants may be in the form of complexes that contain divalent metal ions, including calcium ions (Gotoh *et al.* 2016). Other measures to remove surfactants from wastewater include flotation (including electroflotation), ion exchange, sand sorption, and biodegradation (Tripathi *et al.* 2013). Considering the willingness of consumers to purchase more sustainable products, efforts toward using more biodegradable alternatives for detergents must be considered and incorporated into the market even when being more costly (Ortiz *et al.* 2022).

MECHANISMS OF DETERGENCY

This section considers some mechanistic aspects of detergency. These include basic principles of detergency, mechanisms of release for solid-like *vs.* liquid-like dirt, plasticization of dirt, chemical breakdown of dirt, enzymatic action, and dirt redeposition issues.

Detergency Principles

Minimization of interfacial tension

Many studies have shown that the effectiveness of detergent systems is often maximized under conditions leading to a minimization of interfacial surface tension (Salager *et al.* 1979; Dillan *et al.* 1980; Aveyard *et al.* 1985; Srivastava *et al.* 2006; Tanthakit *et al.* 2008, 2010; Do *et al.* 2015; Budhathoki *et al.* 2016; Chanwattanakit *et al.* 2017; Chanwattanakit and Chavadej 2018; Phaodee *et al.* 2020). This makes sense because it is required to create additional exposed surface area each time that a dirt particle or droplet is released from molecular content with a substrate. One makes the working assumption that the minimization of the air-aqueous tension will correspond also to a minimization of energy to create the new solid-aqueous interfacial area that are associated with dirt release.

One can envision the lowering of interfacial tension as being a manifestation of a two-dimensional spreading pressure of a condensed monolayer film of surfactants at an interface (Timmons and Zisman 1968; Mansour and Zografi 2007). It follows that the most effective surfactant systems will be those most strongly attracted to the interface. As depicted in Fig. 21, which represents a detergent system, the interfaces between water and solids or air usually will be populated by tightly packed monolayers of surfactant molecules. In principle, when the spreading pressure becomes almost equal and opposite to the inherent surface tension of pure water, *i.e.* 72 mNm^{-1}, the measured interfacial tension is minimized. Two contributions to spreading pressure can be anticipated. One of them is the pressure exerted by the closely packed tails groups. If, as depicted in Fig. 21, the tail groups are relatively long (*e.g.* 16 or more carbons in the alkyl chain), unbranched, and unsaturated (for instance stearic acid), then a strong self-association within the film can be expected (Kanicky and Shah 2002; Hubbe *et al.* 2020). The cohesive energy due to the London dispersion forces embodied in such a condensed monolayer is about -20 kJ/mole (Zana 1996). This appears to be more than enough to maintain a compressed configuration of the monolayer (Vollhardt and Fainerman 2006).

The second contribution can come from repulsion between adjacent headgroups. When developmental engineers optimize multi-component detergent formulations, including selections of molecular structures and salt concentrations, they are in a sense optimizing the spreading pressures of surfactant films in the system.

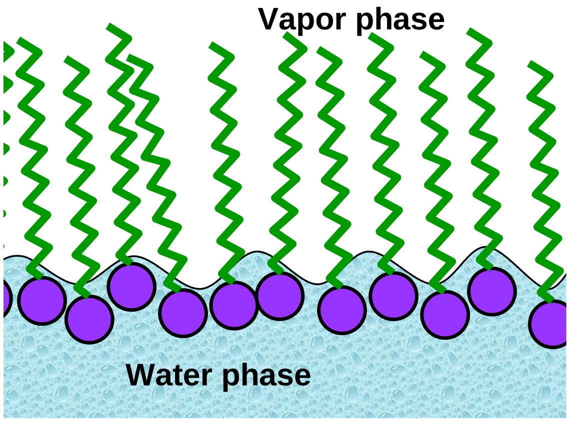

Fig. 21. Schematic diagram of surfactants at an air-water interface, thus creating a film pressure that acts to reduce the net interfacial tension

Surfactant adsorption

The energy of adsorption of surfactants at solid-liquid interfaces or liquid-liquid interfaces can be viewed as an essential aspect in detergency. If the adsorption is strong, then it has the potential to be able to displace a solid or liquid from an attached state. According to Kalak and Cierpiszewski (2015), the effectiveness of a detergent system tends to increase with increasing amount adsorbed, as well as when the rate of adsorption is fast. However, it is important to bear in mind that such energy is not the only important factor. For instance, even though cationic surfactants tend to have high energy of adsorption onto cellulose-based surfaces (Grancarić *et al.* 1997; Alila *et al.* 2005; Penfold *et al.* 2007), they tend not to be the most effective components for detergents.

Surfactant adsorption typically involves sub-monolayer or monolayer filling of surface sites (Paria and Khilar 2004; Paria *et al.* 2005a; Torn *et al.* 2005; Tucker *et al.* 2010; Song *et al.* 2015). When the surfactant concentration is above the CMC, the surface-adsorbed layers likely will be fully populated, as was depicted in Fig. 21. Such phenomena have been most carefully studied with the use of surfactants that are so highly hydrophobic that they can be trapped at the air-water interface. In such systems, monolayers of pure surfactants often can be compressed to solid-like two-dimensional structures in which the molecules are aligned parallel as they are pressed against each other (Vollhardt and Fainerman 2006). The condensed nature of some surfactant layers present at interfaces is evidenced by the fact that detergent binding can be used as a way to quantify surface area (Moller and Lemaire 1993). Such methods, however, depend on either assumptions or knowledge of the packing density of molecules in the monolayer (Holmes and Zeronian 1995; Shen 2002). Cationic surfactants represent an exception to the rule, since they are prone to the formation of bilayers, *i.e.* admicelles, at concentrations above the critical micelle concentration (Muller *et al.* 1998; Alila *et al.* 2005). A sketch of an admicelle was provided earlier in Fig. 9.

Interfacial rigidity

The term interfacial rigidity refers to a compressed monolayer or bilayer of surfactant and its ability to be deformed. In principle, there may be an optimum degree of rigidity to maximize detergency outcomes. It has been shown that interfacial rigidity can be reduced by diluting a pure surfactant in water with a cosurfactant or low-mass lipophilic "linkers" (Salager *et al.* 2005; Acosta *et al.* 2012). Note that a surfactant monolayer will require some flexibility in order to undergo certain mechanisms to be described later (see discussions of the roll-up and snap-off concepts).

Empirical Correlations and Their Relationship to Detergency

A first step in establishing the mechanism by which a process works often lies in the use of correlations. For example, a relationship has been found between the levels of ethoxylation in extended surfactants and the optimum temperatures for detergency (Dillan *et al.* 1979). Detergency generally is negatively correlated with both contact angle and surface tension (Kalak and Cierpiszewski 2015). Wingrave (1984) was able to correlate various aspects of surfactant molecular structure to detergency performance. Some of the concepts that have emerged from such correlations include Winsor conditions (Winsor R ratio), the phase inversion temperature (PIT), the hydrophilic-lipophilic balance (HLB), and the hydrophilic-lipophilic deviation (HLD).

Winsor conditions

Researchers who have mixed oils and surfactants in water systems have noticed trends in phase separation. Photographs showing the Winsor conditions have been provided, for instance, by Salager *et al.* (2013). Because of density, there will often be an oil phase situated above a water phase, but the situation becomes more complex once the amounts of surfactants become significant. Figure 22 illustrates typical phase behavior of mixtures of water and hexadecane, with temperature on the vertical axis and surfactant concentration (an alkyl ethoxyl surfactant) on the horizontal axis (Azemar *et al.* 1993). As shown, two phases exist not only in the absence of surfactant, but also when the temperature is either higher or lower than an optimal range. A third phase, called the Winsor III phase, emerges at an optimum concentration of surfactant. This phase consists of a microemulsion, which has a high ability to accommodate both water and oil. The presence of such a phase has been correlated to highly effective detergency conditions (Azemar *et al.* 1993; Tongcumpou *et al.* 2003a,b, 2005; Tanthakit *et al.* 2008; Phan *et al.* 2010; Salager *et al.* 2013; Kalak and Cierpiszewski 2015; Chanwattanakit and Chavadej 2018; Phaodee *et al.* 2020). At sufficiently high surfactant conditions, the entire mixture may be converted to single phase, as long as the temperature remains in a suitable range. Tongcumpou *et al.* (2003a,b) described a "supersaturation region" close to the transition from a type I to a type III Winsor condition; in that region the microemulsion can become highly swollen with oil, which can be effective for detergency. The most favorable conditions for detergency often can be described as a Winsor I system, although not far from the predicted optimum formulation. The reason is that a high solubilization ability is needed, in combination with a very low concentration of surfactant. Thus, an ideal system will have swollen micelle-like domains (Forgiani *et al.* 2021; Salager *et al.* 2022).

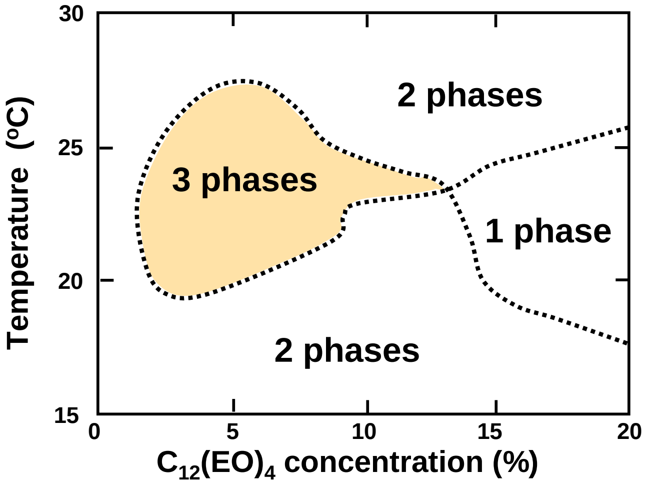

Fig. 22. Typical dependency of number of Winsor phases on temperature and concentration of a nonionic surfactant in water-oil mixtures. Data from Azemar *et al.* (1993) for a system optimized with addition of 0.2 M sodium citrate

Phase inversion temperature (PIT)

During the development of detergent systems, the phase inversion temperature (PIT) can be used as a guide for optimization. This approach can be especially advantageous when attempting to design systems to work at specified temperatures. Raney *et al.* 1987) observed maximum oil solubilization and oil removal near to the PIT. Thompson (1994) observed a similar maximum in detergency at the PIT condition, but another kind of maximum in the curves seemed to follow a different relationship. In Fig. 10, which appeared earlier, the phase inversion temperature was shown as the bold horizontal plotted line.

Hydrophilic-lipophilic balance (HLB)

It has been found that the hydrophilic-lipophilic balance (HLB) of a surfactant is often correlated with maximum detergency performance (Thompson 1994; Tongcumpou *et al.* 2003a). The HLB is a practical measure of the how hydrophilic in character a given surfactant is (Davis 1994). This can be determined by comparing the molecular mass of a hydrophilic group (*e.g.* ethylene oxide) with a hydrophobic group (*e.g.* a saturated alkyl chain). The equation to compute HLB, in such cases, is

$$\text{HLB} = 20 \times M_h / M \quad (1)$$

where M_h is the molecular mass of the hydrophilic group and M is the molecular mass of the whole molecule. In general, a surfactant with a relatively high HLB value is needed to suspend droplets of oily dirt in an aqueous medium (Davis 1994). As noted by Tongcumpou *et al.* (2003a), it is possible to achieve a suitable HLB by adjusting the proportions of two contrasting surfactants. Such binary mixtures are often more robust in terms of providing effective washing over a range of conditions. As noted by Thompson (1994), one can expect maxima in detergency performance associated with the phase inversion condition and with the value of HLB. The usage of pairs of contrasting surfactants can make it possible to achieve conditions well suited for either the roll-off or the snap-off mechanisms of oil release.

Hydrophilic-lipophilic deviation (HLD)

Binary mixtures of surfactants have become widely used in detergent formulations (Rosen and Murphy 1986; Tongcumpou *et al.* 2003a,b; Paria and Khilar 2004; Paria *et al.* 2005a,b; Kaewpukpa *et al.* 2008; Salager *et al.* 2013; Pukale *et al.* 2017). To help optimize such systems, the hydrophilic-lipophilic deviation (HLD) has been defined according to Eq. 2 (Salager *et al.* 2013),

$$\text{HLD} = \ln S - K(\text{EACN}) - f\,(\text{A}) + \sigma - \alpha_T\,(\Delta T) \quad (2)$$

where S is the salinity in wt% of NaCl in the aqueous phase, K is a constant based on the type of head group of the surfactant, EACN is the equivalent alkane carbon number, $f(A)$ is a function of the type and concentration of alcohol, σ is a characteristic parameter of the surfactant, and ΔT is the difference in temperature relative to the reference temperature, *e.g.* 25 °C. This equation makes it possible to optimize mixed solvent systems (Hammond and Acosta 2012; Do *et al.* 2015; Budhathoki *et al.* 2016; Phaodee *et al.* 2020, 2021).

Curvature

When a specified pure surfactant self-assembles at the interface between an oil phase and an aqueous phase, there is often a preferred curvature. The concept was illustrated by Hammond and Acosta (2012) based on the effective diameters of the headgroups *vs.* the tails of selected surfactants. The concept is illustrated in Fig. 23.

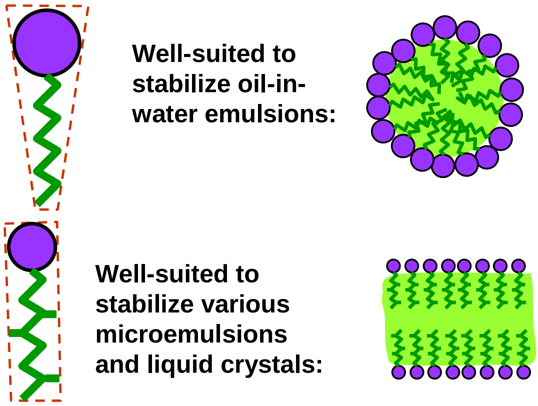

Fig. 23. Illustration of the concept of curvature, whereby the relative sizes of head and tail groups of the surfactant can determine the most favorable type of stabilized systems

When the headgroups are larger, the system is suitable for stabilization of water-in-oil emulsions. By contrast, when the headgroups are narrower than the tail groups, the resulting curvature of the surfactant monolayer would tend to stabilize oil-in-water emulsions. In principle, increasing salinity tends to decrease the effective diameter of an ionically charged headgroup due to screening of electrostatic repulsion forces by the ions in the solution. Detergency is often optimized when the salinity is adjusted such that the effective diameters of the headgroups and tail groups are nearly the same. In other words, the minimum interfacial tension coincides with a curvature of zero (Strey 1996). Acosta *et al.* (2003) proposed a mathematical model to determine the best conditions for solubilization of oils in microemulsions. Zarate-Muñoz *et al.* (2016) showed that the phase inversion point and the surfactant parameter of commercially available alkyl ethoxylate nonionic surfactants can be determined by carrying out tests over ranges of salinity values.

Additives to Tune Microemulsion Performance

Lipophilic linker

The concept of using lipophilic linker compounds in detergent formulation (Graciaa *et al.* 1993; Salager *et al.* 1998; Acosta *et al.* 2012) can be regarded as being a precursor to the later concept of extended surfactants. In each case, the modification can contribute to a less abrupt transition from the hydrophobic end of the surfactants and the hydrophilic ends. Whereas an extended surfactant may have an ethylene oxide sequence inserted between an alkyl group and a sulfate group, the linker can be the same kind of compound without the polar head group (Miñana-Perez *et al.* 1995). The inclusion of lipophilic linkers has been shown to improve detergent performance (Tongcumpou *et al.* 2003a). According to Forgiarini *et al.* (2021), the lipophilic linkers generally have produced more significant effects in comparison to their hydrophilic counterparts.

Alcohol additives

Phaodee *et al.* (2019) showed that the performance of a detergent formulation could be improved by the addition of well-chosen alcohols. In this case the effect was attributed to the softening of semisolid dirt. In combination with an optimization of salinity, the alcohol helped detergency. Heptanol and octanol gave the best results. Other researchers also have reported the use of alcohols in detergent formulations (Salager *et al.* 1979; Scheuing and Hsieh 1988; Miller and Raney 1993; Florescu *et al.* 2009; Tanthkit *et al.*

2010; Pukale *et al.* 2017). In addition, the HLD concept, as described earlier, involves a factor related to alcohol type and content (Witthayapanyanon *et al.* 2008).

Release Mechanisms for Solid-like Particles

The mechanisms related to the release of particulate dirt are not necessarily different from those governing the release of liquid-like dirt, but it is convenient to consider idealized situations. Some authors have stated that solid-like particle can represent a particular challenge to remove during laundering (Gotoh 2010). Two concepts will be considered in this section. The first is a rolling mechanism, by which motion is initiated by hydrodynamic forces. The second is also induced by hydrodynamic forces, but it is based on a shear-induced progressive invasion of detergent components into the contact zone between dirt and substrate. Also to be considered are situations in which the particles are physically entrapped within textile structures.

Rolling release

It has been reported that larger solid particles tend to be removed from textile surfaces at lower levels of agitation compared to smaller ones (van Roosmalen *et al.* 2003; Rojvoranun *et al.* 2012b). Such results are consistent with earlier fundamental studies (Cleaver and Yates 1992; Hubbe 1984, 1985; Mahe *et al.* 1988). It has been proposed that the critical step in the dislodgement of a solid particle is often related to a critical torque needed to initiate a rolling motion (Hubbe 1984). In the cited work, this mechanism was shown to be consistent with the effects of changing the particle size of spherical TiO_2 particles adhering to cellulose or glass planar surfaces. The average shear stress was used to calculate the hydrodynamic torque necessary to initiate a rolling motion under conditions favoring colloidal adhesion between the surfaces. The critical torque required for particle detachment was accounted for in terms of a sum of the van der Waals and electrostatic forces acting between the surfaces (Hubbe 1987). Figure 24 depicts the balance between hydrodynamic torque and adhesive torque that was able to account for the size-dependency of the critical shear stress in that work. In this figure, τ_o* represents the critical shear stress just sufficient to start a rolling motion in the mechanism governing detachment, and *R* is the radius of the particle. The characteristic average distance *l* from the centerline of adhesion to the most important prominent point of roughness resisting attachment was assumed to be proportional to the square-root of radius.

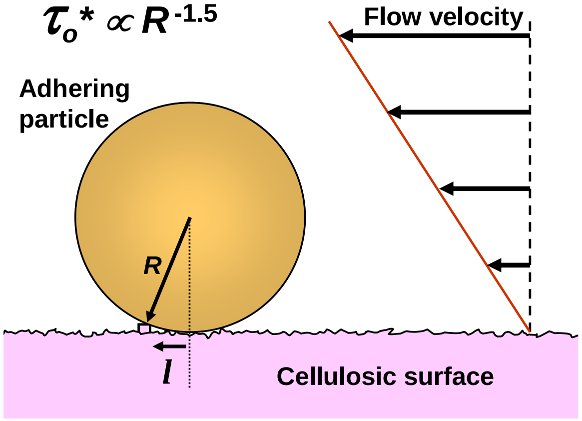

Fig. 24. Idealized model leading to demonstration of a mechanism for dislodgement of spherical particles from flow surfaces exposed to turbulent shear flow (Hubbe 1987)

Banerjee *et al.* (2012a) noted that a ten-fold higher fluid-dynamic force will likely be required under certain laundering situations with supercritical CO_2 due to a stronger contribution of van der Waals forces to adhesion. In support of that concept, Sutanto *et al.* (2014) found that such actions as ultrasound or stirring were ineffective in removal of particles from surfaces during high pressure CO_2 dry cleaning.

The hydrodynamic environment during conventional laundering will almost always involve turbulent flow. To predict what happens during particle dislodgement, it has been proposed that adhering particles will be small enough to be present within a viscous sublayer of such flow adjacent to solid surfaces (Cleaver and Yates 1973; Hubbe 1985). Such a model makes it possible to account for effects of time, since there will be a probabilistic distribution of maximum shear stress associated with "bursts" of flow intensity acting parallel to the surface to which particles are attached (Wilmarth 1975; Hubbe 1985). Consistent with this concept, it has been found that pulsating flow can be much more effective in dislodging particles during laundering in comparison with steady flow (van der Donck 1999).

As a related mechanism, it is also likely that some of the torque needed to initiate a rolling motion of attached dirt particles may be mechanical in nature. As noted earlier, a rubbing motion has been mentioned as a likely cause of particle dislodgement (Yun *et al.* 2017). These researchers set up equipment to simulate the effects of a traditional washboard used in laundering. In interpreting their results it is not clear whether the actual forces imposed on the particles were due to direct mechanical pushing or hydrodynamic in nature.

Solid-like dirt present on textiles does not necessarily resemble the ideal spherical particles employed in some fundamental studies (Hubbe 1985). Rather, the dirt may result from the solidification of material that had been spread as a film (Do *et al.* 2015; Chanwattanakit *et al.* 2017, 2019; Chanwattanakit and Chavadej 2018). In such cases, the attached dirt may have a low profile, and it may not be susceptible to rolling detachment.

Progressive adsorption and stabilization

The hydrodynamic forces and torques just described are likely to act in combination with the action of detergent components. Accordingly, it makes sense to consider evidence that the hydrodynamic stresses, which may be intermittent, play a role in allowing surfactant molecules to enter into the adhesion zones between attached dirt particles and fabric surfaces. This concept is illustrated in Fig. 25. There is a cooperative tendency of surfactant molecules to self-associate with those already present within a monolayer film at an interface (Penfold *et al.* 2007; Hubbe *et al.* 2020). This tendency can be expected to contribute to a progressive extension of such films within adhesion zones between dirt and textile. Even if the wobbling motions induced by intermittent hydrodynamic forces in turbulent flow (Cleaver and Yates 1973; Hubbe 1985) are not by themselves sufficient to dislodge the particles, they might be sufficient to promote diffusion of surfactants into critical locations. Indeed, it has been shown that turbulent flow can promote detergency effects (van der Donck 1997; Warmoeskerken *et al.* 2002; Lee *et al.* 2008; Yun *et al.* 2017). Furthermore, once the detergent molecules have coated all of the surfaces of dirt particles, redeposition onto the textiles becomes less likely.

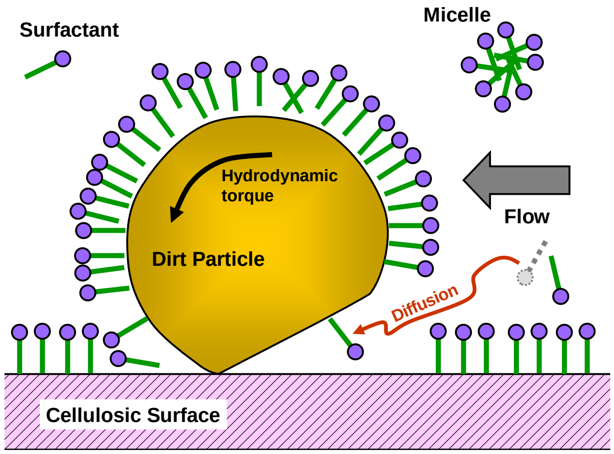

Fig. 25. Schematic illustration of mechanism by which intermittent hydrodynamic forces may facilitate invasion of surfactant molecules into adhesion zone between dirt and fabric even if the hydrodynamic torque is insufficient by itself to dislodge the dirt

The involvement of electrostatic forces relative to the release of particles or droplets from textile surfaces has been supported by experimental observations. In particular, zeta potential of surfaces has been correlated with the effectiveness of detergent systems (Powney and Wood 1940a,b; Luxbacher *et al.* 2008; Rojvoranun *et al.* 2012b). In principle, increasing absolute value of zeta potential (usually having a negative sign) is expected to weaken and then reverse the net adhesion force between the surfaces (Hubbe 1984; Visser 1995; Hubbe and Rojas 2008).

Dislodgement from entrapped state

Release of solid particles can be much more difficult when they are physically entrapped within the structure of fibrils or lumens within a textile material (Schott 1969; Kissa 1981; Obendorf 2004). In addition to the mechanical entrapment, such locations also may be protected from the influence of hydrodynamic forces (Bueno *et al.* 2019). Thus, Obendorf (2004) observed that the physically entrapped dirt was likely to remain in the textiles after laundering. Figure 26 illustrates three limiting cases relative to the location of a dirt particle in a cellulosic fibrillar structure.

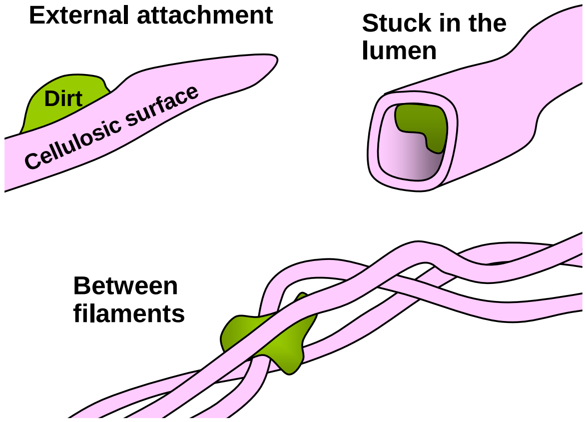

Fig. 26. Contrasting placements of dirt particles on or within cellulosic structures

Bueno *et al.* (2019) considered two categories of location of particles or other dirt entities within textiles. These were termed “inter-yarn” and “intra-yarn”. As noted by Carroll (1993), it is reasonable to expect dirt to be able to reach such locations due to the flexing of clothing during usage. Chi and Obendorf (1999) found that used motor oil was able to penetrate throughout the structure of cotton cloth, and they attributed this to the presence of dispersant additives, *i.e.* surfactants, in the oil. Murata *et al.* (1991) showed that sebum soil, released from human skin, was present in inter-fiber spaces of textiles. Follow-up work showed that such entrapped sebum could be easily removed by alkaline protease enzymatic treatment (Murata *et al.* 1993).

Changes in the shapes and spaces within textile materials during flexing and stretching, during a laundering process, can be expected to help dislodge entrapped dirt particles (Warmoeskerken *et al.* 2002). Accordingly, van der Donck (1997, 1999) considered the stresses acting during the compression of a plug of wet textile. Stretching of the textile appeared to play a role in the release of particles (van der Donck 1999). Yun *et al.* (2013) showed that complex motions of the textiles were especially effective in release of dirt, and this is consistent with the concept of deformation of the material. Carroll (1993) proposed a mechanism by which physical movement of textile surfaces may cause transfer of dirt from one surface to an adjacent surface, possibly leading to ultimate detachment.

Shin *et al.* (2018) proposed that dirt particles might be removed from surfaces by their diffusion in a gradient of surfactant concentration. The proposed mechanism was related to diffusiophoresis. This proposal needs further examination. Gradients in concentration are likely to last for only short times following the addition of surfactant to a washing machine.

Release Mechanisms for Liquid-like Soiling

When the dirt on a textile surface behaves like a liquid, some other mechanisms of detachment can be considered. This includes roll-up detachment and snap-off detachment. In addition, the dirt might become solubilized and transported in micellar form. As noted by Gotoh (2005) and Chanwattanakit *et al.* (2017), often a change in temperature can make the difference between solid-like dirt and liquid-like dirt, relative to the mechanisms of laundering.

Roll-up detachment

It is reasonable to expect that a liquid-like surface of dirt ought to be subject to change in shape as a result of interaction with components of a detergent. This is the basis of the roll-up mechanism of dirt release in response to surfactant action (Dillan *et al.* 1979; Miller and Raney 1993; Thompson 1994; Tongcumpou *et al.* 2005; Sonesson *et al.* 2007; Lee *et al.* 2008; Kalak and Cierpiszewski 2015; Chanwattanakit *et al.* 2017; Phaodee *et al.* 2020). Figure 27 provides a schematic illustration of the roll-up mechanism. As shown, one envisions a mechanism by which progressive completion of a surfactant monolayer at the interface between the aqueous phase and the oily dirt causes it to acquire a spherical shape and to have diminished contact with a solid surface. Ultimately, such a process can result in release of dirt into the aqueous system.

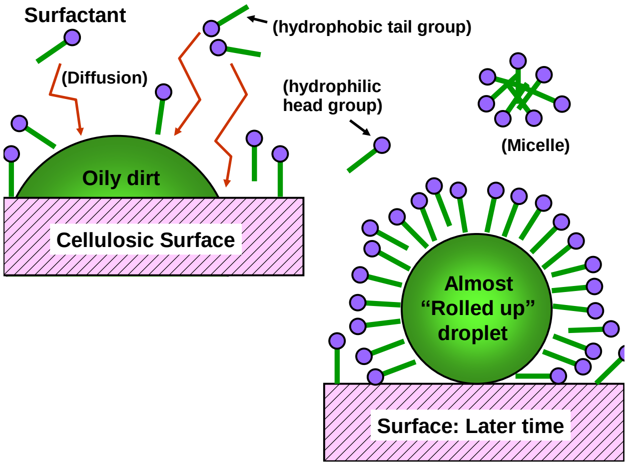

Fig. 27. Schematic illustration of the roll-up mechanism of removal of liquid-like material from a fabric surface during laundering

As explained by Tongcumpou *et al.* (2005), surfactant adsorption adjacent to an attached oil droplet may cause a progressive increase in the contact angle of the drop until it is easily dislodged from the surface. Ren *et al.* (2012) used fluorescence microscopy to show the rolling up process of oil droplets from single cotton fibers. As noted by Dillan *et al.* (1979), the roll-up mechanism of detachment is maximized by lowering the interfacial tension by suitable formulation of the detergent mixture at the temperature and concentration of usage. The concentration of surfactant, even above the critical micelle concentration (CMC), was found to be important (Dillan *et al.* 1980). Han *et al.* (2015) observed that mechanical action was effective in promoting the roll-up detachment of oily dirt from cotton fabric. Such as dependency is consistent with the concept of progressive adsorption of surfactants within adhesion zones, as introduced in the previous section.

As one element in an inherently complex mechanism, there seems to be a logical connection between the curvature concept noted earlier (Acosta *et al.* 2003; Hammond and Acosta 2012) and the roll-up mechanism. In principle, if a surfactant system is optimized to favor the development of oil-in-water emulsion droplets, due to the relative sizes of surfactant headgroups and tail groups, then such a system ought to be favorable for a roll-up mechanism of detachment. Further research will be needed to support such a contribution to the roll-up mechanism.

Snap-off detachment

When textile surfaces are sufficiently hydrophobic, the roll-up mechanism may become ineffective. The hydrophobic dirt material may be too compatible with the surface for the surfactant to be able to penetrate the interfacial zone. In such cases, a mechanism known as snap-off may become dominant, especially for liquid materials (Chanwattanakit *et al.* 2017; Phaodee *et al.* 2020). Tanthakit *et al.* (2010) used high-speed photography to directly show the snap-off process for the detachment of palm oil from a cotton-polyester fabric blend. Figure 28 provides a schematic illustration of the mechanism.

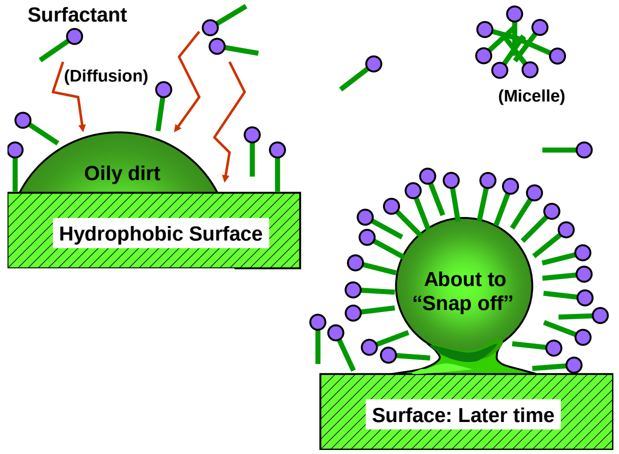

Fig. 28. Schematic illustration of the snap-off mechanism of removal of liquid-like material from a fabric surface during laundering

As shown, the snap-off mechanism involve a necking of the oily material, which is facilitated by the inducement of a very low interfacial tension by the detergent (Dillan *et al.* 1980). Once the necking is complete, the droplet snaps off and gets carried away by the wash liquid. However, the process in never completely efficient due to the fact that part of the oil is always left behind, following snap-off (Dillan *et al.* 1980).

Solubilization

Liquid-like dirt materials can be expected to be susceptible to solubilization through the action of various surfactants, reagents, or enzymes. The effects of surfactants appear to involve a balance between the ability of the surfactant to become incorporated into the soil material and a subsequent contribution to drawing water molecules into the dirt (Scheuing and Hsieh 1988). The cited authors showed a case in which a more hydrophilic surfactant had a greater detergency effect than a more hydrophobic version, despite the fact that the more hydrophobic entity was put more quickly into the oily material.

Micellar transport

Solubilization appears to be a main mechanism to account for the strong detergent activity of systems that contain microemulsions (Kalak and Cierpiszewski 2015). The results reported by the following authors support such a relationship (Dillan *et al.* 1979, 1980; Salager *et al.* 1979; Carroll 1981; Acosta *et al.* 2003; Tongcumpou *et al.* 2003a, 2005; Srivastava *et al.* 2006; Kaewpukpa *et al.* 2008; Tanthakit *et al.* 2009, 2010; Do *et al.* 2015; Attaphong and Sabatini 2017; Chanwattanakit and Chavadej 2018; Phaodee *et al.* 2020). Miller and Raney (1993) stated that solubilization is mainly related to the presence of either a microemulsion or a liquid crystal phase within the detergent mixture.

The more general term "solubilization-emulsification" can be used when describing what takes place as oily material is being removed from a textile surface during laundering (Miller and Raney 1993). Figure 29 presents a concept of solubilization and emulsification of dirt as proposed by Kissa (1987). As shown, the mechanism is envisioned as a series of steps involving a cellulosic surface that is exposed to a detergent solution. At the top left, a micelle composed of surfactant molecules diffuses to the substrate surface. The intermediate affinity of the cellulose favors a surfactant orientation having the tails facing towards or draping on the cellulose surface, while the headgroups face the aqueous phase, *i.e.* a hemimicelle. If and when a hydrophobic particle is present on the surface, it will tend to become incorporated into such a hemimicelle, as shown. Next, it was proposed that the roll-up mechanism, as described earlier, would take place, resulting in release of the stabilized emulsion droplet into the aqueous phase.

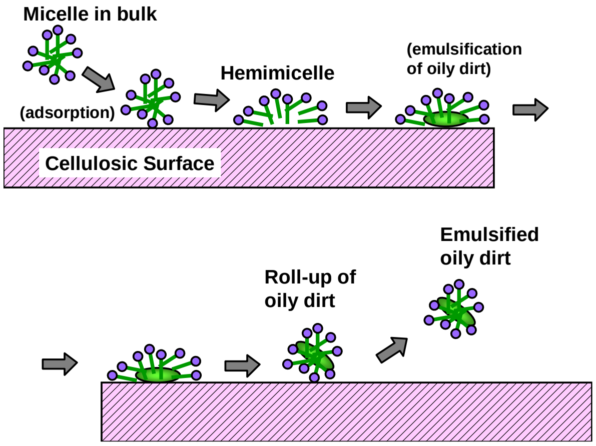

Fig. 29. Concept to explain the emulsification and release of hydrophobic particles by adsorption of micelles, development of hemimicelles, incorporation of oily material, roll-up of the emulsion droplet, and release into the wash water

In principle, emulsification implies that droplets of oil are each solubilized by micelles formed with surfactant molecules (Fig. 29). The term emulsification, as used in the following articles, appears to be more related to the nature of the entities in which oil is removed from textile surfaces, rather than the mechanism of the release itself (Powe 1963; Raney *et al.* 1987; Kawase *et al* 1991, 1994; Carroll 1981, 1993; Miller and Raney 1993; Borchardt 1994; Thompson 1994; Gotoh 2005; Srivastava *et al.* 2006). This oil removal mechanism is more favorable at Winsor I condition (near to Winsor III), favoring oil removal higher than 90% (Phaodee *et al.* 2019, 2020, 2021)

Plasticization of Dirt

The term plasticizer refers to various monomeric and low-mass polymer compounds that tend to increase the fluidity of materials when intimately mixed. By changing the fluidity, such agents have potential to influence the detergency process. Figure 30 shows how the addition of an effective plasticizer can be expected to change the stress-strain behavior of a material. In the case of the non-crystalline regions of polysaccharide-based materials, including cellulosic fibers, water is known to have a plasticizing effect (Back *et al.* 1983; Olsson and Salmén 2004). For example, the storage modulus of hemicellulose decreases moderately with increasing humidity (RH) up to about 72%, and thereafter it decreases in a precipitous manner with further increases to an RH of 90% (Olsson and Salmén 2004). Related work showed that various non-aqueous plasticizers can have similar effects on the properties of cellulose fibers and paper made from them (Salmén *et al.* 1984). Various alcohols have been used in laundry detergent systems, in which they may play the role of plasticizer (Salager *et al.* 1979; Banerjee *et al.* 2012a; Phaodee *et al.* 2019). Chanwattanakit *et al.* (2017) presented evidence that surfactants also can play a similar role by penetrating into the particles and making them more fluid-like.

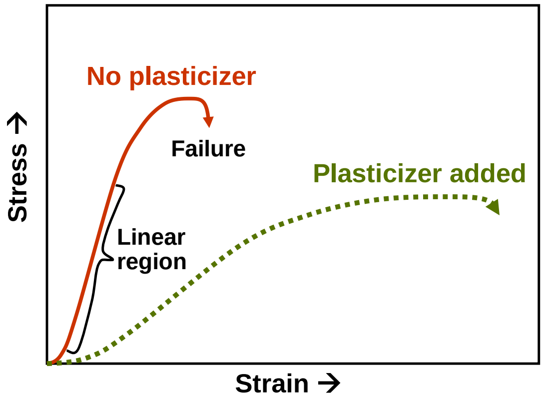

Fig. 30. Expected effects of plasticizer content on the stress-strain behavior of a solid polymeric material

Softening is another word that has been used to denote various monomeric compounds that may affect liquid-like dirt, possibly leading to its removal from surfaces. Again, the idea is to make the material more liquid-like. Cox *et al.* (1987) proposed a softening mechanism for the removal of sebum. The word "liquefaction" was suggested as a synonym for softening in such situations. Borchardt (1994) proposed that removal of oil-based ink from cellulosic fiber surfaces, during the de-inking of paper pulp, involves softening of solid-type inks. Because the word "soften" also can refer to either the binding of Ca^{2+} and Mg^{2+} ions or providing a softer feel to a laundered textile item, it is recommended to use terms such as plasticizing and plasticizer for the effects described here.

Chemical Breakdown of Dirt

Another way to bring about the softening of dirt, as a means to promote detergency, is to break it down chemically. In principle, that often can be achieved by saponification and by oxidation. Saponification involves treatment with alkali so as to convert carboxylic acids to their deprotonated form (Gotoh 2005). Sufficiently intense conditions, in terms of temperature and pH, can also convert carboxylic esters to carboxylate groups, which contribute to solubility in water (Glass 1971). Oxidation, which also can promote the hydrophilic nature of cellulosic materials, can be brought about by such bleaching agents as sodium hypochlorite and catalytic bleaching (Topalović *et al.* 2007; Henniges and Potthast 2009).

Enzymatic Action

An earlier section discussed the inclusion of various types of enzymes in detergent formulations. Some issues related to the mechanisms of enzyme usage in laundering will be considered here, especially with respect to the cellulase family of enzymes.

An important mechanistic question is whether or not the catalytic function of enzymes is always required in order to provide significant improvements in detergency. That question was answered most effectively in the research of Silva *et al.* (2012). Those authors deactivated the catalytic activity of one batch of an esterase. The deactivated enzyme was shown to be about equally effective in the removal of fat from a cotton surface during laundering. The great advantage, in the case described, was that it was possible to avoid the rancid smells that develop when using the active version of the same enzyme. The results also showed that molecular recognition, *i.e.* the action of binding domains of enzymes, can play a key role in detergency.

As mentioned earlier in this article, there is evidence that the presence of surfactants can render enzymes more effective (Traore and Buschle-Diller 1999; Seo *et al.* 2011; Lou *et al.* 2018). Figure 31 suggests three mechanisms to account for such enhancement. Lou *et al.* (2018) attributed this to a protection by the surfactant against deactivation of the enzymes. In the absence of surfactant, cellulase was found to become deactivated in the presence of agitation. The presence of a nonionic surfactant appeared to make the system resistant to the unfolding of the protein structure of the enzyme. In contrast, Seo *et al.* (2011) suggested that the enhancement in enzyme action was due to increased swelling and accessibility of cellulose surfaces in wood material. A third proposed mechanism is related to the ineffective binding of cellulase to lignin (or other hydrophobic moieties), rendering it unavailable for enzymatic hydrolysis of cellulose (Berlin *et al.* 2005; Arslan *et al.* 2016). Presumably, the presence of surfactant can ease the detachment of enzyme from such sites, thereby allowing it to be more effective in its enzymatic activity (Wang *et al.* 2013; Fritz *et al.* 2015). However, this mechanism has been called into question by some recent work (Lee *et al.* 2021).

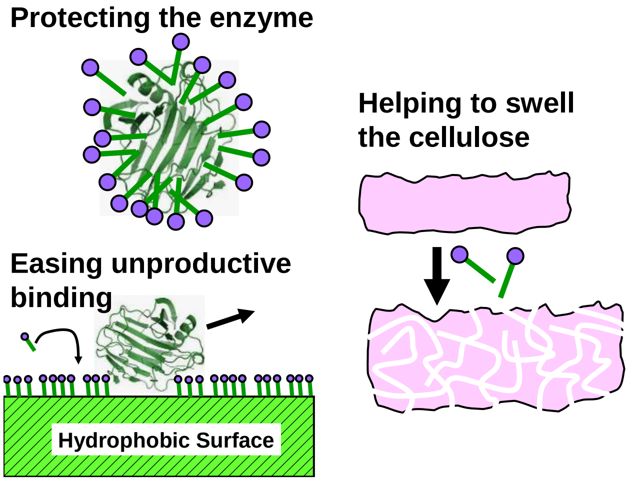

Fig. 31. Three mechanisms that have been proposed to account for beneficial effects of enzyme treatment on detergency

Dirt Redeposition Issues

The next stage in a typical laundering cycle, after the usage of detergent, is a rinsing stage. An immediate effect of adding rinse water to a laundry batch is a decrease in the concentrations of the components of the detergent formulation, including the surfactants. An expected consequence is that the concentration may fall below the critical micelle concentration, which can lead to a decrease in the colloidal stability of suspended particles of dirt. As shown in Fig. 32, there may be further concerns regarding whether there is enough dispersant present to impart sufficient negative charges on surfaces to resist redeposition of the dirt. Various researchers have reported significant redeposition of dirt onto fabrics during this vulnerable part of the process (Powney and Wood 1940a; Sanders and Lambert 1950; Huggins and Langguth 1968; Chanwattanakit *et al.* 2019). Chanwattanakit and Chavadej (2018) observed that most of the dirt removed during laundering is in non-solubilized form, *i.e.* either solid particles or emulsion droplets. Bubl (1970) observed minimal redeposition of sebum and clay in the case of cotton cloth specimens that were washed in parallel experiments at six university laboratories.

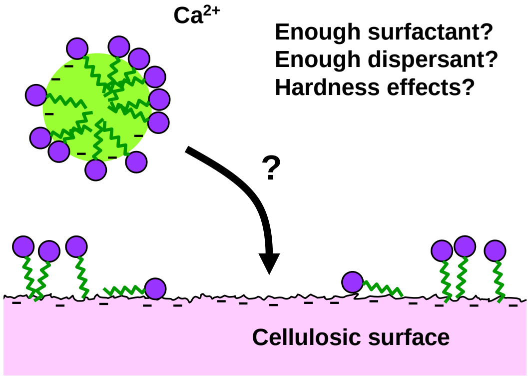

Fig. 32. Some concerns relative to the possible redeposition of direct, especially during the rinsing stage of laundering

The redeposition process generally can be understood according to the principles of colloidal chemistry (Visser 1995). Thus, the likelihood of a sticking collision between a dirt particle and a wetted surface of cloth, within the aqueous mixture, will be governed by a balance of forces. The attractive forces usually can be described as van der Waals attractions, in combination with the hydrophobic effect described earlier (Tanford 1980). Figure 33 shows a traditional representation of how the net free energy of interaction between particles, as a function of distance, often can be attributed to a balance between van der Waals (London dispersion) attractions and electrical double layer repulsions.

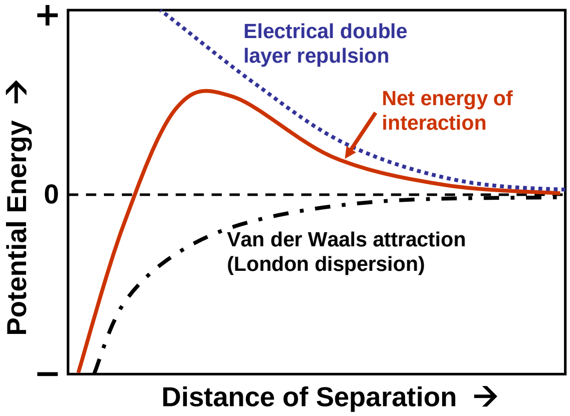

Fig. 33. Net interaction energy between surfaces, as a function of distance, according to a conventional Derjaguin-Landau-Verwey-Overbeek (DLVO) concept

To confer resistance to redeposition of dirt, two components of repulsive force can be used. One approach is to render all of the surfaces negatively charged. Detergent components including phosphates (acting in their role as dispersants), sodium carboxymethylcellulose, acrylate copolymers, and even anionic surfactants can contribute to the needed negative surface change (Powney and Wood 1940a; Chanwattanakit *et al.*

2017). In non-aqueous media, including pressured liquid CO_2, it is more difficult to achieve charge stabilization due to the instability of ions in such media (Banerjee *et al.* 2012a). The other component of repulsive force is called steric stabilization (Napper 1977; Hubbe and Rojas 2008; Rojvoranun *et al.* 2012a), which involves chains of hydrophilic polymer extending from the surfaces into the aqueous phase. Coagulation and deposition are inhibited in such situations. The nonionic surfactants involving ethylene oxide chains can be effective in this regard. Various studies have shown the effectiveness of nonionic surfactants in the overall effectiveness of detergent system (Rojvoranun *et al.* 2012a; Chanwattanakit *et al.* 2019). Rojvoranun *et al.* (2012a) found that steric stabilization was an effective way to minimize redeposition of dirt back onto laundered items during rinsing. Chanwattanakit *et al.* (2019) observed more serious redeposition problems at higher temperatures of laundering due to the ability of softened or liquefied dirt to penetrate into protected areas within fabric yarns. Sanders and Lambert (1950) observed the greatest amount of redeposition in detergent systems lacking any builder, such as phosphate. Gotoh (2016) observed more redeposition of soot and olive oil with increasing hardness of the water. Sutanto *et al.* (2013) found that it was helpful to add some cellulosic material to a laundry batch subjected to supercritical CO_2. The cellulosic material appeared to coat the textile fibers, rendering the surfaces more hydrophilic and less suitable for redeposition of various kinds of dirt.

CELLULOSE-RELATED STRATEGIES FOR DETERGENCY

This section considers cellulose-related strategies to enhance various effects of detergency. Subtopics will include strategies based on the chemical characteristics of cellulose, strategies based on the microstructure of cellulosic yarns and fibers, aspects related to the durability of cellulose-based materials, and future prospects related to cellulosic resources and their usage in detergency.

Strategies Based on the Cellulose Chemical Characteristics

Swelling and hydration

Cellulose and some of its derivatives share some inherent features, such as hydrophilic character, which can be used advantageously to promote detergency. Key issues in this regard are how to best take advantage of the hydrogen bonding tendency, and to a lesser extent the development of negative ionic charge at some cellulosic surfaces under neutral to alkaline conditions. The strong tendency for water molecules to interact with cellulosic surfaces may help to explain the relative ease with which some types of dirt are removed from cotton and other cellulose-based articles (Kissa 1981; Gotoh 2005; Tanthakit *et al.* 2008). Kissa (1981) proposed that the diffusion of water to the dirt-fiber interface is a key factor in initiating the roll-up mechanism of release of dirt. This mechanism is illustrated schematically in Fig. 34. One can envision the water molecules, in the course of adding detergent solution to a washing machine, interposing themselves between the cellulosic fabric and various dirt entities and starting a process of displacing the dirt from the surfaces. The energy of formation of an individual hydrogen bond in water is about 21 kJ/mole, which is over 20 times lower than a covalent bond between O and H in water. However, that energy is still about a factor of ten larger than the ubiquitous London dispersion component of van der Waals forces that cause attraction between all matter at close range (Visser 1995).

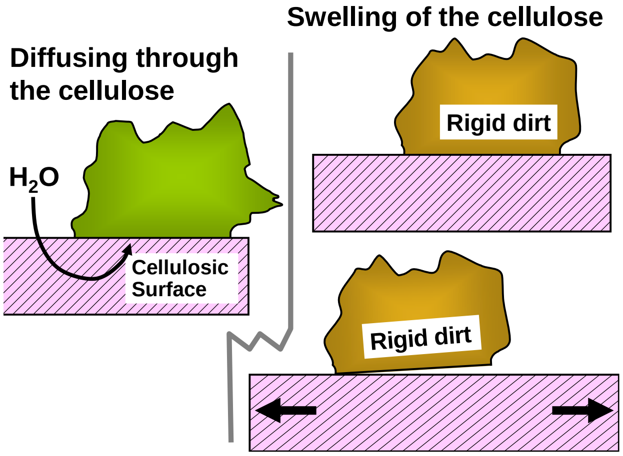

Fig. 34. Two mechanisms by which the characteristics of cellulose (water permeability and tendency to swell when wetted) may contribute to the detachment of dirt

In principle, the tendency of cellulosic materials to swell in the course of wetting by water can be used as a mechanism to aid in the release of relatively inflexible dirt layers. Thus, the swelling of a substrate, adjacent to an inflexible material, would be expected to create shear stress at the interface, leading to slippage and separation. This mechanism can help to explain the dislodgment of toner flakes from xerographically printed paper upon its resuspension in water (Borchardt 1994). As noted by Doelker (1993), not all cellulose derivatives swell in water; for instance, high levels of esterification render the material hydrophobic and non-swelling in water. The diffusion and interaction of water with cellulosic materials within amorphous regions provides an initial tendency for swelling of those regions (Aulin *et al.* 2009; Kontturi *et al.* 2011). It has been shown, for instance, that a thin film of cellulose having a high content of amorphous character swelled to about twice its original dry thickness when wetted (Kontturi *et al.* 2011).

The fact that cellulosic materials tend to swell more in water with increasing pH has been attributed to the deprotonation of carboxyl groups (Grignon and Scallan 1980; Chang *et al.* 2011). Osmotic pressure develops when ionic groups are attached within cellulosic material, especially when the aqueous solution has low ionic strength (Grignon and Scallan 1980). Notably, many detergent formulations contain salts, such as sodium sulfate (Azemar *et al.* 1993; Eken-Saracoglu and Culfaz 1999; Tongcumpou *et al.* 2003a; Acosta *et al.* 2012; Phaodee *et al.* 2020). Such salinity in the water can be expected to depress the osmotic pressure, resulting in less swelling of the suspended material. In addition, discharge of salt-containing water to streams and lakes is undesirable. Thus, there will be a continuing motivation to decrease the salt content of detergent formulations (Tongcumpou *et al.* 2003a). Torn *et al.* (2005) found evidence that at low concentrations three different nonionic surfactants adsorbed with both the tails and headgroups lying down on cellulose. At higher concentrations (presumably near or above the CMC), lateral self-association became dominant, leading to surface agglomerates, *i.e.* hemimicelles.

Surfactant interactions

In a similar manner to the suggesting “wedging” effect of water molecules moving to a dirt-substrate interface, one might envision a parallel role for surfactants at cellulosic interfaces. As was noted earlier in this article, the combination of surface-active nature and a tendency for mutual association between adjacent surfactant molecules in a condensed monolayer (Biswas and Chattoraj 1997; Penfold *et al.* 2007) can be expected to have an elbowing effect at the edges of dirt-cellulose interfaces. In the case of cellulosic substrates, however, there is reason to doubt the importance of such a mechanism. Due to the relatively hydrophilic nature of relatively pure cellulosic surfaces, typical surfactant molecules would not be expected to have a very high energy of adsorption. Strongly hydrophobic areas on such substrates can be expected only in the presence of substances such as wax (Ginn *et al.* 1961). A contrary view was expressed by Paria *et al.* (2005b), who argued that cellulose can be better described as having both hydrophilic and hydrophobic sites. Anionic and nonionic surfactants were proposed to favor the hydrophobic sites (presumably with the hydrophobic tails facing or lying upon the hydrophobic areas), and cationic surfactants were proposed to favor the hydrophilic sites. Such a view is consistent with the work of Yamane *et al.* (2006), who found highly contrasting affinity characteristics of regenerated cellulose, depending on the polar or nonpolar nature of the regenerating baths. The cited authors presented models of two different crystal faces of pure cellulose to justify such a view. It was argued that when cellulose is regenerated in a polar liquid, the numerous –OH groups that are arranged equatorial in the anhydroglucose repeating structure of cellulose will be facing outwards. By contrast, those groups would tend to face inwards, presenting a more hydrophobic surface, when the cellulose is regenerated in non-polar media. It is not known, however, how these concepts would apply to such surfaces as cotton. Simoncić and Roman (2007) observed that adsorption of both nonionic and anionic surfactants onto cotton tended to render those surfaces more hydrophilic; such observations are consistent with the hydrophobic tail groups predominantly oriented toward the cellulose.

Enzymatic interactions

The ability of a cellulase enzyme to attach strongly to cellulosic surfaces may contribute to the release of dirt. The situation seems analogous to the roll-up mechanism of detergent action, whereby the self-association of surfactant molecules and their strong tendency to migrate to interfaces effectively create a wedging force at the three-phase zone between dirt, substrate, and the aqueous phase. However, there are many unclear aspects related to how enzymatic binding domains might participate in such wedging action. For instance, the binding of enzymes is often regarded as static in specific locations, rather than crawling progressively across the surface of a substrate. If a cellulase binding domain had a tendency to migrate across a cellulosic surface, then it would then be easy to understand how such action could serve as a wedge to push way dirt that happens to be in the way of the enzyme molecule. It makes logical sense that exocellulase enzymes, which mainly detach cellobiose groups from the ends of cellulose chains, would keep working on a given chain, progressively removing more end-groups (Shibafuji *et al.* 2014). Likewise, observations by Silva *et al.* (2012) can be regarded as evidence that factors such as the thermal motions within enzyme structures provide a tendency for them to traverse across the surfaces such as cellulose, possibly following the fibrillar directions. The proposed mechanism is supported by atomic force microscopy imaging of cellulase enzyme movements along cellulose crystal surfaces (Zhang *et al.* 2016). Further evidence suggests that such cellulase action may be focused on the hydrophobic faces of cellulose crystals (Liu *et al.* 2011).

A related mechanistic question concerning the workings of enzymes concerns the reversible or irreversible nature of the adsorption. Notably, Caparrós *et al.* (2012) observed reversible adsorption of a cellulose binding domain (CBD) onto cellulose by one type of cellulase and irreversible adsorption by another. The cited authors further observed that mechanical action appeared to be important during the detergent action. Such a dependency suggests that the pulsations of flow might be a contribution to the lateral progression of cellulase across the surface of a cellulose-based substrate. This could, in principle, contribute to a mechanism by which the translocation of enzymes across a textile surface might shove dirt particles or films out of the way.

Another mechanistic question is whether the actual cleavage of cellulose microfibrils by enzymes plays a significant role in enzyme-promoted detergent action. For example, Li and Hardin (1998) observed that surfactants, mechanical action, and the selection of enzymes were important for the scouring of cotton. The authors were especially concerned with the removal of wax and related materials from cotton surfaces, thus rendering the cotton more hydrophilic. The fact that cellulase can be effective in this regard can be taken as evidence that the enzyme chews up some of the fibrils that are acting as tethers to attach the wax or other hydrophobic materials to the surfaces. Such a mechanism would also be consistent with the demonstrated effectiveness of some cellulase systems in promoting the release of offset printing inks from cellulosic fiber surfaces during the de-inking of fibers from recovered printed paper (Borchardt 1994).

Sizing of textile fibers with hydrophilic materials

In the preparation of fibers for textile applications, it is conventional practice to apply materials to the fiber surfaces, *i.e.* sizing (Goswami *et al.* 2004; Djordjević *et al.* 2014). One commonly used sizing agent, according to Goswami *et al.* (2004), is carboxymethylcellulose (CMC), a cellulose derivative. Often the main purpose of sizing is to facilitate processing of the fibers in the manufacture of cloth. The material on the surface can adjust the frictional properties of the filaments to be able to maintain consistent tension and to avoid breakage of filaments during processing. Treatments related to such functions as permanent press also can be added at a stage after the cloth has been manufactured (Rhee *et al.* 1993a). Though laundering tends to remove some of the sizing materials, some sizing agents and surface treatments of textiles may remain after many cycles (Rhee *et al.* 1993a; Goswami *et al.* 2004). For example, acrylic acid may be employed as a soil-release agent (Obendorf 2004).

As a means of making some other fabric compositions more closely resemble cellulose with respect to their laundering properties, it would make sense to coat them with nanocellulose (Lavoine *et al.* 2012; Lindström 2017). These materials generally can be described as disorganized networks of cellulosic fibrils having diameters in the range of about 10 to 100 nm. Ideally, the nanocellulose would be administered to fabric surfaces together with a suitable bonding agent such as polyamidoamine-epichlorohydrin resin (Espy 1995; Lu *et al.* 2020), which could be heat-cured during the drying process after sizing of threads or after preparation of the cloth.

Strategies Based on the Porous Nature of Cellulosic Yarns

Cellulosic fiber materials often can be described as porous on microscopic and submicroscopic levels. The pores are present between the yarns of textiles, between filaments within yarns, as lumen spaces within such fibers as cotton, and within fiber cell walls and regenerated cellulose as mesopores. Except for some of the mesopores, all of these spaces are large enough to accommodate detergent components such as surfactant molecules and even enzymes. Accordingly, one can envision the detergent components diffusing through the pores of the cellulosic material to reach the points of attachment for the dirt. Studies have shown that the susceptibility of cellulosic material to enzymatic breakdown is often limited by the size of available channels that might provide access to cellulase (Jeoh *et al.* 2007; Bansal *et al.* 2009).

Though it is theoretically possible for surfactant and enzyme molecules to reach critical locations in the textile material based on a diffusion mechanism, such a process would be unacceptably slow. Fortunately, laundry operations invariably involve agitation, which provides a basis for convection as a main contribution to the movement of surfactants and other detergent components through the material. The compliant and elastic nature of wet cellulosic material is consistent with the action of squeezing as a mechanism by which flow is induced in and out of pores within the material. The chaotic flows and squeezing actions during conventional laundering have been shown to be particularly effective with respect to detergency (van der Donck 1997; Warmoeskerken *et al.* 2002; Lee *et al.* 2008; Yun *et al.* 2017).

Flow as a tool for release

In addition to providing a means for rapid convective transport of detergent components to sites of attachment of dirt, flow also will provide forces and torques that can be instrumental in detachment. Some aspects of these mechanisms may be specific to cellulosic materials. In particular, the fibrillar and mesoporous nature of common cellulosic textile materials imply that many dirt particles or droplets will be somewhat protected from hydrodynamic forces (Bueno *et al.* 2019). In that regard, the manner of flow has been shown to make a difference. Muir *et al.* (2013) observed that flow directed through cotton fabrics was more effective in dirt removal compared to cross-flow.

Durability of Cellulose-based Textiles *vs.* Detergents

Fiber wear and damage during laundering

The age of a material can be measured in terms of the time elapsed since its formation, as well as the time elapse since its glass transition temperature was first exceeded. Thus, it is important to consider the impact of laundering on fiber wear (Rathinamoorthy and Raja Balasaraswathi 2020). Contributing factors, such as the compactness of the fabric structure (weave or knit), yarn twist, yarn form (staple fiber or filament), and even fabric thickness and basis weight will have a direct effect on the extent of fiber shedding during the wash. However, the laundering process itself was found to be responsible for most of the damage to textile products, which also explains why a garment’s shelf life is usually measured by its ability to withstand a certain number of washes (Rathinamoorthy and Raja Balasaraswathi 2020).

While both polyester and cellulose-based textiles shed the most fibers from all fiber categories, cellulosic textiles surpass synthetics in the volumes of microfibers released during laundering. It’s been reported that cellulosic-based textiles released 0.2 to 4 mg microfibers/g fabric, compared with 0.1 to 1 mg microfibers/g fabric released by polyester textiles (Zambrano *et al.* 2019).

According to Zambrano *et al.* (2019), the process of microfiber generation involves multiple steps: fuzz formation, swelling, fibrillation, pill formation, and pill wear-off. These steps are illustrated in an idealized fashion in Fig. 35. Whereas the figure envisions a stepwise process, it should be understood that the steps might proceed simultaneously. They also proposed that shedding of the individual textile is governed by how easily the fibers can be broken off due to the washing machine’s mechanical action before forming the pill, which ultimately constitutes the fuzz formation step. Broken staple fibers are responsible for most of the microfiber formation and shedding (Zambrano *et al.* 2019).

Shedding is also the term that Rathinamoorthy and Raja Balasaraswathi (2020) used to describe the release of fibers during laundering, describing the action of loose or damaged fibers detaching from the surface or the edges of a textile. There have been no concrete studies done to more deeply investigate the mechanism behind shedding, although some studies identify mechanical stress, resulting from the textile surface's abrasion, to be the leading cause. Additionally, chemicals may lead to fiber degradation, including during washing via the use of a detergent, which could dissolve some components of the fibers, leading to further fiber disengagement from the surface. As one of the main roles of a detergent is the removal of dirt and the prevention of re-deposition from the surface of the fabric, it could also possibly affect fiber fragments by acting as a dispersing agent, essentially keeping the microfibers away from the fabric (Rathinamoorthy and Raja Balasaraswathi 2020).

It is difficult to assess the exact impact of detergent on fiber shedding. Some studies have found that use of detergent resulted in more fiber shedding, due to reduced friction on the fiber surface, as well as an increased pH; others showed quite the opposite – that detergent use actually reduced fiber shedding, specifically in synthetic fibers. However, due to the lower surface tension of the liquid and better wettability of the fiber with detergent use, cellulosic fibers still experienced more fiber shedding (Rathinamoorthy and Raja Balasaraswathi 2020). On the other hand, Zambrano *et al.* (2019) mentioned that synthetic microfibers, which have a low surface energy, will react more strongly with non-polar organic chemicals than their cellulose-based counterparts (Zambrano *et al.* 2019).

A garment can release between 1900 and 11,000 of fibers during one wash. Overall, for all fiber types, fiber shedding during laundering was found to increase as a result of detergent or softener use, temperature increase, washing machine type, number and duration of wash cycles, and material to liquid volume ratio. According to Zambrano *et al.* (2019), water temperature during laundering plays an especially significant role in the increase of cellulosic microfiber shedding, as increased temperature is said to promote swelling in cellulosic fibers, freeing up space for broken fibers to disengage from the textile. The shear forces during wash enhance fuzz formation on the swollen textile. Similarly, Rathinamoorthy and Raja Balasaraswathi (2020) mentioned that, unlike with synthetic fibers, washing temperature is an important factor for cellulosic fibers, as it is said to negatively impact shedding as it increases. They explained that it is caused by the decrease of mechanical strength in cellulose, as it swells and loses fiber fragments (Rathinamoorthy and Raja Balasaraswathi 2020; Zambrano *et al.* 2019).

While the volume of fiber shedding in cellulosic fibers is the highest amongst all fiber categories, it is notably of least concern due to its biodegradable nature (Rathinamoorthy and Raja Balasaraswathi 2020). It is known that microplastics are present in fiber-like form in the large volumes of wastewater effluents discharged to water bodies globally. While cellulosic microfibers were also found in wastewater effluents, it was found that the majority of the fibers were composed of polyester, especially polyethylene terephthalate (PET). As this type of fiber is one of the most common in the textile industry, it is believed that these microfibers enter the water through washing machine effluents; they constitute 35% of total volume of microplastics released to the ocean (Zambrano *et al.* 2019).

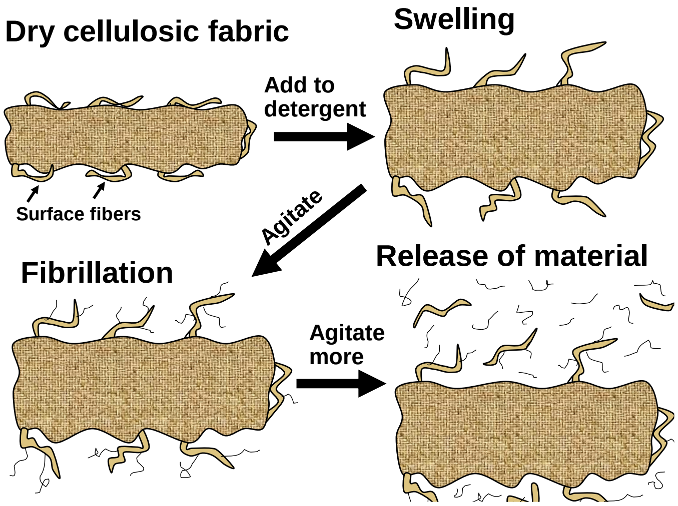

Fig. 35. Idealized mechanism of microfiber release from cellulose-based textiles and yarns (as cited in Zambrano *et al.* 2019)

Efforts have been made to address the release of microfibers into wastewater effluents in washing machines by the proposal of several innovative filtration systems, such as Lint LUV-R filter, GUPP-YFRIEND washing bag, or the Coral ball. However, these solutions were unsuccessful in capturing fibers with length lower than 150 to 200 µm, which are the majority of fibers shed during laundering (Zambrano *et al.* 2019).

Additionally, while there are no set criteria to certify a material as biodegradable in aquatic or marine environments, testing methods such as ISO 14851:1999 can be used to measure aerobic aquatic biodegradability of microfibers. According to Zambrano *et al.* (2019), the ISO 14851:1999 testing method was used to measure aquatic biodegradability of 100% cotton, 50%cotton/50%polyester, 100% polyester, and 100% rayon knitted fabrics in activated sludge solids (simulating natural aquatic environments). After 243 days, cotton reached 75.9 ± 12.4% biodegradability and rayon reached 62.2 ± 13.3% biodegradability, after the subtraction of nitrification interferences. Therefore, both cellulose-based textiles were deemed to be aerobically biodegradable in an aquatic environment, partially thanks to their lower crystallinity and higher moisture regain. However, while the concern about the impact of cellulosic microfibers in the aquatic and marine evnironments is minimal, the lack of literature available on this topic is nevertheless concerning, and there is an additional need to understand the flow of these microfibers, and to help improve their future removal from wastewater effluents (Zambrano *et al.* 2019).

Destructive effects of enzymes

One of the drawbacks of using enzymes in detergents is that excessive concentration or inadequate temperature may cause unwanted damage to the cellulosic substrate. As one example, Rahman *et al.* (2021) found significant decreases in tensile strength on lyocell (39.0%) and cotton (27.5%) fabrics after cellulase hydrolysis performed at 60 °C. This finding was supported by results from the original detergent formulations with cellulases, which were acid enzymes at a pH level of 5. These were substantially abrasive enzymes, which considerably reduced the cellulosic textile’s tensile strength during washing, simultaneously resulting in high amounts of redeposition. Neutral cellulases, with a pH of ~6.5 to 7.0, are normally preferred in detergent use, but they are also more costly. Additionally, it is recommended that cellulase performance should be studied at different levels of mechanical agitation to understand ultimate impact of combination of the enzyme's abrasion and the mechanical action on the cellulosic textile (de Souza Moreira *et al*. 2016).

Similarly, Olsen and Falholt (1998) pointed out that repeated exposure to "color clarification cellulases," which help fabrics regain and maintain clear colors, surface smoothness and softness, can result in significant damage to cotton product. This damage initially presents itself as loss of fabric strength and excessive softening of fabric edges or hems. Such harm can be usually prevented by balancing the dosage of cellulase in detergent (Olsen and Falholt 1998).

Damage to laundered items has been reported with respect to the usage of bleaching agents (Li *et al.* 2012). The cited authors found that some of the C6 groups in the anhydroglucose units of cellulose were prone to oxidation by the bleach. Pusić *et al.* (2008) tracked the effects of bleach by measuring the streaming potential of the cotton fibers and blends. As might be expected, oxidation by bleaches during laundering also can attack the colorants in garments, especially if the bleach concentration is high (Oakes 2005).

High pH, which is used in some industrial washing system, might be expected to damage some fabrics. Takahashi *et al.* (2007) observed relatively little damage to cotton fabrics during laundering at high, especially in comparison to wool.

Future Prospects Related to Cellulosic Resources

This section considers possible roles of cellulose and its byproducts in future developments related to detergency. Areas of interest include builders, enzyme-based systems, formulations for cold-water detergency, and bio-based surfactant development.

Effective builders (CMC)

As noted earlier, carboxymethylcellulose (CMC) has potential to be used as a builder in detergent formulations (Vaughn and Smith 1948; Agarwal *et al.* 2012). Though polycarboxylated species can be expected to have a strong tendency to bind divalent ions, such as Ca^{2+}, the degree of substitution of typical CMC products is lower than that of other polymeric builders, such as polyacrylate products (Komaki *et al.* 2002; Milojević *et al.* 2013). However, it appears that the ability to bind hardness ions is not the only factor involved. The fact that microcrystalline cellulose (MCC) shows promising effects, when used as a replacement for other builders (Agarwal *et al.* 2012), suggests that these types of products may be functioning as anti-redeposition aids. In that respect, a primary function of MCC may be to provide surface area upon which various dirt components can become fixed, allowing much of it to be removed with rinse water. In addition, cellulosic material in a detergent formulation has the potential to serve as an adsorbent for dyes that may have been released from fabric to the aqueous phase (Vivod *et al.* 2019). There is also a need for research to find out whether CMC varieties having a higher degree of substitution might be more effective as builders.

Enzymatic assist (binding domains, options)

The fact that detergency of cellulose-based textiles can be promoted by the use of cellulase enzymes (Aaslyng *et al.* 1990; Murata *et al.* 1991, 1993; Hoshino *et al.* 2000; Obendorf 2004) reveals important information about the mechanism of detergency and opens up the door for further developments. Two likely mechanisms appear to merit follow-up research. First, the effectiveness of cellulases in releasing dirt from fabrics can be regarded as evidence that a substantial proportion of dirt materials become bound to nano-size cellulosic fibrils at fabric surfaces. Such a mechanism would support a practice of sizing textile surfaces with nanocellulose, as suggested earlier. Depending on how strongly the nanocellulose were bound to the surface, it could either be enzymatically hydrolyzed or simply mechanically detached from the surface, thus causing the associated dirt to be released as well from the textile surfaces. Second, while not as applicable to purely cellulosic fiber textiles, the use of detergents containing cellulase enzymes was found to significantly reduce the pilling normally caused by fabric softeners after 10 wash cycles or more. This is an area of opportunity for cellulosic and synthetic fiber blends, as this application of the cellulase enzyme was found to be especially successful in blended fiber fabrics (Hernandez *et al.* 2017).

Cold-water detergent systems (minor components)

Regardless of what other trends emerge in coming years, it appears that cold-water washing technology will remain a topic of emphasis. Present detergent systems for cold-water washing, though showing great promise, still need to be improved. Cellulosic materials may be expected to serve functions as builders and anti-redeposition aids, as already suggested in this article. In addition, it is important not to overlook the mechanical aspects of washing processes. Solid particles such as microcrystalline cellulose (MCC) in a detergent mixture might possibly contribute to mechanical scouring in an agitated system (Mazurek *et al.* 2001; UhZapata *et al.* 2022). The word “scouring” is being used in the cited articles in the sense that suspended particles are being used to increase abrasive action at surfaces exposed to flow. Notably, Carroll (1993) proposed that mechanical action may cause an oily droplet intermittently to contact another surface and become transferred. By such means it is reasonable to expect that dirt from a fabric might be transferred to cellulose-based particles suspended in the washing medium.

Bio-based detergents (fatty acid components)

Due to its low cost, hydrophobic nature, and its suitability for attachment of hydrophilic groups, there has been interest in the development of surfactants based on lignin (Uraki *et al.* 2012; Sipponen *et al.* 2019). In particular, sodium lignosulfonate is a low-cost surfactant byproduct of the sulfite pulping of wood (Rueda *et al.* 2015; Tarasov *et al.* 2015). Sodium lignosulfonate has been shown to be effective in such applications as enzymatic saccharification of lignocellulose (Wang *et al.* 2013; Zhou *et al.* 2013), and the preparation of polyurethane foams (Hatakeyama *et al.* 2003). Ou *et al.* (2017, 2021) grafted alkylglycidyl ether and 3-chloropropionic acid onto alkaline lignin. The resulting surfactant showed promise as a detergent component for cotton fiber. Best results were obtained when mixing the bio-based surfactant with a conventional sodium dodecyl benzene sulfonate surfactant (Ou *et al.* 2021). The effectiveness of detergency of the new surfactant exceeded that of ordinary lignosulfonate (Ou *et al.* 2017).

Release of microplastics into the environment

Hernandez *et al.* (2017) pointed out that roughness had the most impact on the propensity for fibers to break away from the textile. They also noted that cellulosic fibers, such as viscose, were more prone to break down, lint, and pill as a result of aging, unlike synthetic fibers, such as polyester, which tended to remain intact in the textile structure. Nevertheless, laundering can result in a large number of fibers being released into the environment (Hernandez *et al.* 2017). Cellulosic microfibers have been found in wastewater effluents (Zambrano *et al.* 2019), most likely entering the water through washing machine effluents; and they constitute 35% of total volume of microplastics released to the ocean. Unfortunately, existing filtration systems in washing machines are incapable of capturing fibers with length lower than 150 to 200 μm (Zambrano *et al.* 2019). On the other hand, Rathinamoorthy and Raja Balasaraswathi (2020) noted that while the volume of fiber shedding in cellulosic fibers is the highest amongst all fiber categories, it is of least concern due to its biodegradable nature (Rathinamoorthy and Raja Balasaraswathi 2020). Cellulose-based materials were found to be aerobically biodegradable in an aquatic environment, partially thanks to their lower crystallinity and higher moisture regain (Zambrano *et al.* 2019). Nevertheless, there is a need to further understand the flow of these microfibers, and to help improve their future removal from wastewater effluents or prevent them from entering the water bodies as a result of laundering.

CONCLUDING REMARKS

Based on the literature cited in this article, it is clear that cellulosic materials have played a substantial role in detergency in many applications. Part of the story begins with the widespread usage of cotton and rayon, as well as their blends, in textile products. In addition, cellulose and various derivatives of cellulose can function detergent components, for example as builders and anti-redeposition aids. Additionally, innovative cellulose-based strategies have been shown to significantly influence detergency performance. Relatively recent developments in detergent systems include cold-water systems and the usage of cellulose-hydrolyzing enzymes. Given the relatively rapid developments in such technologies, as well as others touched upon in this review, there appears to be substantial need for continuing research in the field of detergency in systems that contain cellulose.

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REFERENCES CITED

Aaslyng, D., Gormsen, E., and Malmos, H. (1990). "Mechanistic studies of proteases and lipases for the detergent industry," *J. Chem. Technol. Biotech.* 50(3), 321-330. DOI: 10.1002/jctb.280500304

Acosta, E. J., Kiran, S. K., and Hammond, C. E. (2012). "The HLD-NAC model for extended surfactant microemulsions," *Journal of Surfactants and Detergents* 15(4), 495-504. DOI: 10.1007/s11743-012-1343-2

Acosta, E., Szekeres, E., Sabatini, D. A., and Harwell, J. H. (2003). "Net-average curvature model for solubilization and supersolubilization in surfactant microemulsions," *Langmuir* 19(1), 186-195. DOI: 10.1021/la026168a

Aehle, W. (2007). *Enzymes in Industry: Production and Applications*, Wiley-VCH. DOI: 10.1002/9783527617098

Agach, M., Marinkovic, S., Estrine, B., and Nardello-Rataj, V. (2016). "Acyl poly(glycerol-succinic acid) oligoesters: Synthesis, physicochemical and functional properties, and biodegradability," *Journal of Surfactants and Detergents* 19(5), 933-941. DOI: 10.1007/S11743-016-1853-4

Agach, M., Marinkovic, S., Estrine, B., and Nardello-Rataj, V. (2018). "Biosourced lauroyl poly(glycerol-succinate) oligoesters modified by copolymerizable solvents: A wasteless and eco-friendly surfactants properties enhancement," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 536, 88-95. DOI: 10.1016/J.COLSURFA.2017.07.033

Agarwal, C., Ilindra, A., and Karadbhajne, V. (2012). "Carboxymethyl cellulose versus microcrystalline cellulose in the manufacturing of liquid detergents," *Indian J. Chem. Technol.* 19(2), 149-151.

Akcabay, D. T., Dowling, D. R., and Schultz, W. W. (2014). "Clothes washing simulations," *Computers Fluids* 100, 79-94. DOI10.1016/j.compfluid.2014.05.005

Al-Ghanayem, A. A., Joseph, B., Alhussaini, M. S., and Ramteke, P. W. (2022). "Current applications and future trends of extremozymes in detergent Industries," *Microbial Extremozymes* 2022, 223-230. DOI: 10.1016/b978-0-12-822945-3.00020-8

Alila, S., Boufi, S., Belgacem, M. N., and Beneventi, D. (2005). "Adsorption of a cationic surfactant onto cellulosic fibers. I. Surface charge effects," *Langmuir* 21, 8106-8113. DOI: 10.1021/la050367n

Alila, S., Aloulou, F., Beneventi, D., and Boufi, S. (2007). "Self-aggregation of cationic surfactants onto oxidized cellulose fibers and coadsorption of organic compounds," *Langmuir* 23(7), 3723-3731. DOI: 10.1021/la063118n

Alwadani, N., and Fatehi, P. (2018). "Synthetic and lignin-based surfactants: Challenges and opportunities," *Carbon Resources Conversion* 1(2), 126-138. DOI: 10.1016/j.crcon.2018.07.006

Arslan, B., Colpan, M., Ju, X. H., Zhang, X., Kostyukova, A., and Abu-Lail, N. I. (2016). "The effects of noncellulosic compounds on the nanoscale interaction forces measured between carbohydrate-binding module and lignocellulosic biomass," *Biomacromol.* 17(5), 1705-1715. DOI: 10.1021/acs.biomac.6b00129

Attaphong, C., and Sabatini, D. A. (2017). "Optimized microemulsion systems for detergency of vegetable oils at low surfactant concentration and bath temperature," *J. Surfact. Deterg.* 20(4), 805-813. DOI: 10.1007/s11743-017-1962-8

Aulin, C., Ahola, S., Josefsson, P., Nishino, T., Hirose, Y., Österberg, M., and Wågberg, L. (2009). "Nanoscale cellulose films with different crystallinities and mesostructures-their surface properties and interaction with water," *Langmuir* 25(13), 7675-7685. DOI: 10.1021/la900323n

Auta, H. S., Emenike, C. U., and Fauziah, S. H. (2017). "Distribution and importance of microplastics in the marine environment: A review of the sources, fate, effects, and potential solutions," *Environ. Int.* 102, 165-176. DOI: 10.1016/j.envint.2017.02.013

Aveyard, R., Binks, B. P., Lawless, T. A., and Mead, J. (1985). "Interfacial-tension minima in oil + water + surfactant systems – Effects of salt and temperature in systems containing non-ionic surfactants," *J. Chem. Soc. Faraday Trans. I* 81, 2155-2168. DOI: 10.1039/f19858102155

Awual, M. R. (2019). “Efficient phosphate removal from water for controlling eutrophication using novel composite adsorbent,” *J. Cleaner Product.* 228, 1311-1319. DOI: 10.1016/j.jclepro.2019.04.325

Azemar, N., Carrera, I., and Solans, C. (1993). “Studies on textile detergency at low temperature,” *Dispersion Sci. Technol.* 14(6), 645-660. DOI: 10.1080/01932699308943436

Back, E., Salmén, L., and Richardson, G. (1983). “Transient effects on mechanical properties of paper during sorption of moisture,” *Paperi Puu* 65(12), 801.

Banerjee, S., Sutanto, S., Kleijn, J. M., van Roosmalen, M. J. E., Witkamp, G. J., and Stuart, M. A. C. (2012a). “Colloidal interactions in liquid CO_2 – A dry-cleaning perspective,” *Adv. Colloid Interface Sci.* 175, 11-24. DOI: 10.1016/j.cis.2012.03.005

Banerjee, S., Sutanto, S., Kleijn, J. M., and Stuart, M. A. C. (2012b). “Towards detergency in liquid CO_2 – A surfactant formulation for particle release in an apolar medium,” *Colloids Surf. A – Physicochem. Eng. Aspects* 415, 1-9. DOI: 10.1016/j.colsurfa.2012.10.004

Bansal, P., Hall, M., Realff, M. J., Lee, J. H., and Bommarius, A. S. (2009). “Modeling cellulase kinetics on lignocellulosic substrates,” *Biotech. Adv.* 27(6), 833-848. DOI: 10.1016/j.biotechadv.2009.06.005

Benson, H. L., Cox, K. R., and Zweig, J. E. (1985). “Nonionic-based detergent systems for cold water cleaning,” *Soap Cosmetics Chem. Spec.* 61(3), 35.

Berg, J. (1992). *Wettability*, Dekker, New York. DOI: 10.1201/9781482277500

Berlin, A., Gilkes, N., Kurabi, A., Bura, R., Tu, M. B., Kilburn, D., and Saddler, J. (2005). “Weak lignin-rinding enzymes – A novel approach to improve activity of cellulases for hydrolysis of lignocellulosics,” *Biochem. Biotech.* 121, 163-170. DOI: 10.1385/ABAB:121:1-3:0163

Bettenhausen, C. (2022). “Switching to sustainable surfactants,” *Chem. Eng. News* May 1. https://cen.acs.org/business/specialty-chemicals/Switching-sustainable-surfactants/100/i15

Bevinakatti, H., and Waite, A. G. (2012). “Surfactant compounds,” US Patent 8,097,564.

Bianchetti, G. O., Devlin, C. L., and Seddon, K. R. (2015). “Bleaching systems in domestic laundry detergents: A review,” *RSC Adv.* 5(80), 65365-65384. DOI: 10.1039/c5ra05328e

Biswas, S. C., and Chattoraj, D. K. (1997). “Polysaccharide-surfactant interaction. 1. Adsorption of cationic surfactants at the cellulose-water interface,” *Langmuir* 13, 4505-4511. DOI: 10.1021/la960905j

Bocquet, L., Charlaix, E., Ciliberto, S., and Crassous, J. (1998). “Moisture-induced ageing in granular media and the kinetics of capillary condensation,” *Nature* 396(6713), 735-737. DOI: 10.1038/25492

Borchardt, J. K. (1994). “Mechanistic insights into de-inking,” *Colloids Surf. A – Physicochem. Eng. Aspects* 88(1), 13-25. DOI10.1016/0927-7757(94)80081-2

Brito, R. O., Silva, S. G., Fernandes, R. M. F., Marques, E. F., Enrique-Borges, J., and do Vale, M. L. C. (2011). “Enhanced interfacial properties of novel amino acid-derived surfactants: Effects of headgroup chemistry and of alkyl chain length and unsaturation,” *Colloids Surf. B – Biointerfaces* 86(1), 65-70. DOI: 10.1016/j.colsurfb.2011.03.017

Broze, G. (1999). *Handbook of Detergents, Part A: Properties*, Marcel Dekker, New York, NY. DOI: 10.1201/b10985

Bubl, J. L. (1970). "Laundering cotton fabric. 1. Effects of detergent type and water temperature on soil removal," *Textile Res. J.* 40(7), 637-643. DOI: 10.1177/004051757004000709

Budhathoki, M., Hsu, T.-P., Lohateeraparp, P., Roberts, B. L., Shiau, B.-J., and Harwell, J. H. (2016). "Design of an optimal middle phase microemulsion for ultra high saline brine using hydrophilic lipophilic deviation (HLD) method," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 488, 36-45. DOI: 10.1016/j.colsurfa.2015.09.066

Budisa, N., and Schulze-Makuch, D. (2014). "Supercritical carbon dioxide and its potential as a life-sustaining solvent in a planetary environment," *Life* 4(3), 331-340. DOI: 10.3390/life4030331

Bueno, L., Laso, C., Amador, C., and Bakalis, S. (2019). "Modelling the kinetics of stain removal from knitted cotton fabrics in a commercial front loader washing machine (FLWM)," *Eng. Sci.* 200, 176-185. DOI10.1016/j.ces.2019.02.008

Burkinshaw, S. M., and Anthoulias, A. (1996). "The wash-off of reactive dyes on cellulosic fibres. 1. Dichlorotriazinyl dyes on cotton," *Pigments* 31(3), 171-193. DOI: 10.1016/0143-7208(96)00010-1

Burkinshaw, S. M., and Katsarelias, D. (1997). "The wash-off of reactive dyes on cellulosic fibres. 2. Monochlorotriazinyl dyes on cotton," *Dyes Pigments* 33(1), 11-31. DOI10.1016/S0143-7208(96)00033-2

Cahn, A., and Feighner, G. C. (1996). "Performance evaluation of household detergents," in: *Soaps and Detergents: A Theoretical and Practical Review*, L. Spitz (ed.), AOCS Press, Champaign, IL, Ch. 13, pp. 381-403.

Caparrós, C., Lant, N., Smets, J., and Cavaco-Paulo, A. (2012). "Effects of adsorption properties and mechanical agitation of two detergent cellulases towards cotton cellulose," *Biocatal. Biotransform.* 30(2), 260-271. DOI: 10.3109/10242422.2012.666840

Carrion-Fite, F. J. (2014). "The detergency of surfactant mixtures and bentonites on cotton fabric," *Tenside Surfact. Deterg.* 51(2), 126-132. DOI: 10.3139/113.110292

Carroll, B. J. (1976). "Accurate measurement of contact-angle, phase contact areas, drop volume, and Laplace excess pressure in drop-on-fiber systems," *J. Colloid Interface Sci.* 57(3), 488-495. DOI10.1016/0021-9797(76)90227-7

Carroll, B. J. (1981). "The kinetics of solubilization of nonpolar oils by nonionic surfactant solutions," *J. Colloid Interface Sci.* 79, 126-135. DOI: 10.1016/0021-9797(81)90055-2

Carroll, B. J. (1993). "Physical aspects of detergency," *Colloids Surf. A – Physicochem. Eng. Aspects* 74(2-3), 131-167. DOI: 10.1016/0927-7757(93)80262-D

Ceballos, D. M., Fellows, K. M., Evans, A. E., Janulewicz, P. A., Lee, E. G., and Whittaker, S. G. (2021). "Perchloroethylene and dry cleaning: It's time to move the industry to safer alternatives," *Frontiers Public Health* 6, article no. 638082. DOI: 10.3389/fpubh.2021.638082

Chan, Y. W., Acquah, C., Obeng, E. M., Dullah, E. C., Jeevanandam, J., and Ongkudon, C. M. (2019). "Parametric study of immobilized cellulase-polymethacrylate particle for the hydrolysis of carboxymethyl cellulose," *Biochemie* 157, 204-212. DOI: 10.1016/j.biochi.2018.11.019

Chang, C. Y., He, M., Zhou, J. P., and Zhang, L. N. (2011). "Swelling behaviors of pH- and salt-responsive cellulose-based hydrogels," *Macromol.* 44(6), 1642-1648. DOI: 10.1021/ma102801f

Chanwattanakit, J., and Chavadej, S. (2018). "Laundry detergency of solid non-particulate soil using microemulsion-based formulation," *J. Oleo Sci.* 67(2), 187-198. DOI: 10.5650/jos.ess17135

Chanwattanakit, J., Scamehorn, J. F., Sabatini, D. A., and Chavadej, S. (2017). "Laundry detergency of solid non-particulate soil or waxy solids: Part I. Relation to oily soil removal above the melting point," *J. Surfact. Deterg.* 20(4), 815-830. DOI: 10.1007/s11743-017-1963-7

Chanwattanakit, J., Scamehorn, J. F., Sabatini, D. A., and Chavadej, S. (2019). "Laundry detergency of solid nonparticulate soil or waxy solids: Part II. Effect of the surfactant type," *J. Surfactants Detergents* 22(3), 571-585. DOI: 10.1002/jsde.12243

Chen, C.-L., Shen, H.-W., Harwell, J. H., and Shiau, B.-J. (2022). "Characterizing oil mixture and surfactant mixture via hydrophilic-lipophilic deviation (HLD) principle: An insight in consumer products development," *Colloids Surf. A. – Physicochem. Eng. Aspects* 634, article no. 127599. DOI: 10.1016/j.colsurfa.2021.127599

Chi, Y. S., and Obendorf, S. K. (1999). "Detergency of used motor oil from cotton and polyester fabrics," *J. Surfact. Deterg.* 2(1), 1-11. DOI: 10.1007/s11743-999-0059-6

Ciabatti, I., Cesaro, F., Faralli, L., Fatarella, E., and Tognotti, F. (2009). "Demonstration of a treatment system for purification and reuse of laundry wastewater," *Desalin.* 245, 451-459. DOI: 10.1016/j.desal.2009.02.008

Cleaver, J. W., and Yates, B. (1973). "Mechanism of detachment of colloidal particles from a flat substrate in a turbulent-flow," *J. Colloid Interface Sci.* 44(3), 464-474. DOI: 10.1016/0021-9797(73)90323-8

Cohen, L., Moreno, A., and Berna, J. L. (1992). "Detergency of binary-mixtures of LAS/STPP and LAS/zeolites – Influence of (Ca^{++}) on the washing liquor," *J. Amer. Oil. Chem. Soc.* 69(7), 678-681. DOI: 10.1007/BF02635809

Conte, J. S., and Bender, G. W. (1992). "Softening and debonding agents," in *Chemical zeoliteProcessing Aids in Papermaking: Practical Guide*, K. J. Hipolit (ed.), TAPPI Press, Atlanta, 167-177.

Cox, M. F., Smith, D. L., and Russell, G. L. (1987). "Surface chemical processes for removal of solid sebum soil," *J. Amer. Oil Chemists Soc*. 64, 273-276. DOI: 10.1007/BF02542017

Cutler, W. G., and Kissa, E. (1987). *Detergency: Theory and Technology*, M. Dekker, New York.

David, A., Singh Chauhan, P., Kumar, A., Angural, S., Kumar, D., Puri, N., and Gupta, N. (2018). "Coproduction of protease and mannanase from *Bacillus nealsonii* PN-11 in solid state fermentation and their combined application as detergent additives," *International Journal of Biological Macromolecules* 108, 1176-1184. DOI: 10.1016/j.ijbiomac.2017.09.037

Davis, H. T. (1994). "Factors determining emulsion-type - Hydrophile-lipophile balance and beyond," *Colloils Surf. A. – Physicochem. Eng. Aspects* 91, 9-24. DOI: 10.1016/0927-7757(94)02929-6

de Carvalho, J. C., Magalhães, A. I., and Soccol, C. R. (2018). "Biobased itaconic acid market and research trends-is it really a promising chemical?," *Chimica Oggi/Chemistry Today* 36(4), 56-58.

Delhomme, C., Weuster-Botz, D., and Kühn, F. E. (2009). "Succinic acid from renewable resources as a C4 building-block chemical—A review of the catalytic possibilities in aqueous media," *Green Chemistry* 11(1), 13-26. DOI: 10.1039/b810684c de Souza Moreira, L. R., Lo Sciuto, D., and Filho, E. X. (2016). "An overview of cellulose-degrading enzymes and their applications in textile industry," *New and Future Developments in Microbial Biotechnology and Bioengineering* 165-175. DOI: 10.1016/b978-0-444-63507-5.00014-9

Dillan, K. W., Goddard, E. D., and McKenzie, D. A. (1979). "Oily soil removal from a polyester substrate by aqueous nonionic surfactant systems," *J. Am. Oil Chem. Soc.* 56, 59-70. DOI: 10.1007/BF02671763

Dillan, K. W., Goddard, E. D., and McKenzie, D. A. (1980). "Examination of the parameters governing oily soil removal from synthetic substrate," *J. Am. Oil Chem. Soc*. 57, 230-237. DOI: 10.1007/BF02673947

Djordjević, S., Kovacević, S., Nikolić, L., Miljković, M., and Djordjević, D. (2014). "Cotton yarn sizing by acrylamide grafted starch copolymer," *J. Natural Fibers* 11(3), 212-224. DOI: 10.1080/15440478.2013.874963

Do, L. D., Attaphong, C., Scamehorn, J. F., and Sabatini, D. A. (2015). "Detergency of vegetable oils and semi-solid fats using microemulsion mixtures of anionic extended surfactants: The HLD concept and cold water applications," *J. Surfact. Deterg.* 18(3), 373-382. DOI10.1007/s11743-014-1659-1

Doelker, E. (1993). "Cellulose derivatives," *Adv. Polym. Sci.* 107, 199-265. DOI: 10.1007/BFb0027554

Dybdahl Hede, P. (2020, May 7). "A beginner's guide to enzymes in detergents," Novozymes. Retrieved June 10, 2022, from https://biosolutions.novozymes.com/en/dish/insights/article/beginners-guide-enzymes-detergents.

Easson, M., Condon, B., Villalpando, A., and Chang, S. C. (2018). "The application of ultrasound and enzymes in textile processing of greige cotton," *Ultrasonics* 84, 223-233. DOI: 10.1016/j.ultras.2017.11.007

Eken-Saracoglu, N., and Culfaz, M. (1999). "Clinoptilolite zeolite as a builder in nonphosphated detergents," *J. Environ. Sci. Health. Pt. A – Toxic/hazard. Subst. Environ. Eng.* 34(8), 1619-1626. DOI: 10.1080/10934529909376916

Eriksson, T., Borjesson, J., and Tjerneld, F. (2002). "Mechanism of surfactant effect in enzymatic hydrolysis of lignocellulose," *Enzyme Microb. Technol.* 31(3), 353-364. DOI: 10.1016/S0141-0229(02)00134-5

Espy, H. H. (1995). "The mechanism of wet-strength development in paper: A review," *TAPPI J.* 78(4), 90-99.

Fanun, M., Makharza, S., and Sowwan, M. (2010). "Transition from micelles to microemulsions in sugar-based surfactant systems probed by fluorescence spectroscopy and atomic force microscopy," *J. Dispersion Sci. Technol.* 31(9), 1212-1219, article no. PII 926083843. DOI: 10.1080/01932690903218153

Fardim, P., and Tikka, P. (2011). *Chemical Pulping*, 2nd Ed, Paper Engineers Assoc., Paperi ja Puu Oy, Helsinki.

Fengel, D., and Wegener, G. (1984). *Wood: Chemistry, Ultrastructure, Reactions*, W. de Gruyter, New York. DOI: 10.1515/9783110839654

Fisher, L. R., and Israelachvili, J. N. (1979). "Direct experimental-verification of the kelvin equation for capillary condensation," *Nature* 277(5697), 548-549. DOI: 10.1038/277548a0

Florescu, S., Cristescu, G., and Leca, M. (2009). "Alternative surfactants for LAS in environmentally friendly detergent compositions," *Revue Roumaine de Chimie* 54(4), 323.

Forgiarini, A. M., Marquez, R., and Salager, J.-L. (2021). “Formulation improvements in the application of surfactant-oil-water systems using the HLD_N approach with extended surfactant structure,” *Molecules* 26(12), article no. 3771. DOI: 10.3390/molecules26123771

French, A. D. (2017). “Glucose, not cellobiose, is the repeating unit of cellulose and why that is important,” *Cellulose* 24(11), 4605-4609. DOI: 10.1007/s10570-017-1450-3

Fritz, C., Ferrer, A., Salas, C., Jameel, H., and Rojas, O. J. (2015). “Interactions between cellulolytic enzymes with native, autohydrolysis, and technical lignins and the effect of a polysorbate amphiphile in reducing nonproductive binding,” *Biomacromol.* 16(12), 3878-3888. DOI: 10.1021/acs.biomac.5b01203

Fujii, T., Tatara, T., and Minagawa, M. (1986). “Studies on applications of lipolytic enzyme in detergency. 1. Effect of lipase from *Candida cylindracea* on removal of olive oil from cotton fabric,” *J. Amer. Oil Chemists Soc.* 63(6), 796-799. DOI: 10.1007/BF02541967

Gardner, D. J., and Tajvidi, M. (2016). “Hydrogen bonding in wood-based materials: An update,” *Wood Fiber Sci.* 48(4), 234-244.

Giagnorio, M., Sotoft, L. F., Tiraferri, A., and Gruttner, H. (2017). “Ultrafiltration to reuse laundering wash water: Evaluation of membranes and permeate flux,” *Desalination Water Treat.* 62, 22-30. DOI: 10.5004/dwt.2017.20133

Ginn, M. E., Kinney, F. B., and Harris, J. C. (1961). “Effect of cotton substrate characteristics upon surfactant adsorption,” *J. Amer. Oil. Chemists Soc.* 38(3), 138-143. DOI: 10.1007/BF02641235

Glass, R. L. (1971). “Alcoholysis, saponification and preparation of fatty-acid methyl-esters,” *Lipids* 6(12), 919-925. DOI: 10.1007/BF02531175

GlobeNewswire (2022). “Laundry detergent market predicted to garner a revenue of $1,03,286.00 million in the 2021-2028 timeframe, growing at a healthy CAGR of 6.70%,” Report by Research Drive, https://www.globenewswire.com/en/news-release/2022/03/30/2412947/0/en/Laundry-Detergent-Market-Predicted-to-Garner-a-Revenue-of-1-03-286-00-Million-in-the-2021-2028-Timeframe-Growing-at-a-Healthy-CAGR-of-6-70-165-Pages-Report-by-Research-Dive.html

Goddard, E. D. (1994). “Polymer/surfactant interaction – Its relevance to detergent systems,” *J. Amer. Oil Chemists Soc.* 71(1), 1-16. DOI: 10.1007/BF02541467

Gong, F., Xu, H., and Dong, J. (2022). “Effect of sodium lignosulfonate on the anti-redeposition ability of cotton cloth in a SDBS-$Na_2C_2O_4$-CMC formulation,” *Tenside, Surfactants, Detergents* 59(3), 221-230. DOI: 10.1515/TSD-2021-2397/MACHINEREADABLECITATION/RIS

Gooijer, H., and Stamminger, R. (2016). “Water and energy consumption in domestic laundering worldwide – A review,” *Tenside Surfact. Deterg.* 53(5), 402-409. DOI: 10.3139/113.110456

Goswami, B. C., Anandjiwala, R. D., and Hall, D. (2004). *Textile Sizing,* CRC Press, New York. DOI: 10.1201/9780203913543

Gotoh, K. (2005). “The role of liquid penetration in detergency of long-chain fatty acid,” *J. Surfactants Detergents* 8(4), 305-310. DOI: 10.1007/s11743-005-0360-4

Gotoh, K. (2010). “Investigation of optimum liquid for textile washing using artificially soiled fabrics,” *Textile Res. J.* 80(6), 548-556. DOI: 10.1177/0040517509340605

Gotoh, K., Horibe, K., Mei, Y., and Tsujisaka, T. (2016). “Effects of water hardness on textile detergency performance in aqueous cleaning systems,” *J. Oleo Sci.* 65(2), 123-133. DOI: 10.5650/jos.ess15168

Gotoh, K., and Mei, Y. (2017). "Effect of washing conditions on cleaning action of linear alkylbenzene sulfonate in hard water," *Tenside Surfactants Detergents* 54(4), 291-298. DOI: 10.3139/113.110502

Gotoh, K., Nakatani, H., and Tsujisaka, T. (2015). "Delicate laundering of textiles with application of 38 Hz ultrasonic waves," *Textile Res. J.* 85(15), 1565-1578. DOI: 10.1177/0040517515569523

Graciaa, A., Lachaise, J., Cucuphat, C., Bourrel, M., and Salager, J. L. (1993). "Improving solubilization in microemulsions with additives. 1. The lipophilic linker role," *Langmuir* 9(3), 669-672. DOI: 10.1021/la00027a010

Grancarić, A. M., Pusić, T., Soljacić, I., and Ribitsch, V. (1997). "Influence of electrokinetic potential on adsorption of cationic surfactants," *Textile Chem. Colorist* 29(12), 33-35.

Grancarić, A. M., Tarbuk, A., and Kovacek, I. (2009). "Nanoparticles of activated natural zeolite on textiles for protection and therapy," *Chem. Ind. Chem. Eng. Quart.* 15(4), 203-210. DOI: 10.2298/CICEQ0904203G

Grignon, J., and Scallan, A. M. (1980). "Effect of pH and neutral salts upon the swelling of cellulose gels," *J. Appl. Polym. Sci.* 25(12), 2829-2843. DOI: 10.1002/app.1980.070251215

Grunewal, W. (1970). "Surfactants in dry-cleaning processes," *Fette Seifen Anstrichmittel verbunden mit der Zeitschrift die Ernahrungsindustrie* 72(3), 189. DOI: 10.1002/lipi.19700720305

Hammond, C. E., and Acosta, E. J. (2012). "On the characteristic curvature of alkyl-polypropylene oxide sulfate extended surfactants," *Journal of Surfactants and Detergents* 15(2), 157-165. DOI: 10.1007/s11743-011-1303-2

Han, H. R., Chung, S. E., Kim, J., and Park, C. H. (2015). "Mechanical and physiochemical contribution in removal of different soil types on cotton fabric," *Textile Res. J.* 85(19), 2009-2019. DOI: 10.1177/0040517515580515

Harwot, P., and van de Ven, T. G. M. (1997). "Effects of sodium oleate and calcium chloride on the deposition of latex particles on an air/water interface," *Colloids Surf. A – Physicochem. Eng. Aspects* 121(2-3), 229-237. DOI: 10.1016/S0927-7757(96)03986-6

Hatakeyama, T., Asano, Y., and Hatakeyama, H. (2003). "Mechanical and thermal properties of rigid polyurethane foams derived from sodium lignosulfonate mixed with diethylene-, triethylene- and polyethylene glycols," *Macromol. Symp.* 197, 171-180. DOI: 10.1002/masy.200350716

Hayes, D. G., and Smith, G. A. (2019). "Biobased surfactants: Overview and industrial state of the art," in: *Biobased Surfactants: Synthesis, Properties, and Applications*, AOCS Press, pp. 3-38. DOI: 10.1016/B978-0-12-812705-6.00001-0

Henniges, U., and Potthast, A. (2009). "Bleaching revisited: Impact of oxidative and reductive bleaching treatments on cellulose and paper," *Restaurator* 30(4), 294-320. DOI: 10.1515/rest.017

Hernandez, E., Mitrano, D. M., and Nowack, B. (2017). "Polyester textiles as a source of microplastics from households: A mechanistic study to understand microfiber release during washing," *Environmental Science and Technology* 51, 7036-7046. DOI: 10.1021/acs.est.7b01750.s001

Herrera, C. G. (1996). "Detergency. Its main mechanisms," *Grasas y Aceites* 47(6), 419-435. DOI: 10.3989/gya.1996.v47.i6.890

Higgins, L., Anand, S. C., Holmes, D. A., Hall, M. E., and Underly, K. (2003). "Effects of various home laundering practices on the dimensional stability, wrinkling, and other properties of plain woven cotton fabrics. Part I: Experimental overview, reproducibility of results, and effect of detergent," *Textile Res. J.* 73(4), 357-366. DOI: 10.1177/004051750307300414

Holmes, S. A., and Zeronian, S. H. (1995). "Surface-area of aqueous sodium-hydroxide hydrolyzed high-speed spun poly(ethylene-terephthalate) fibers," *J. Appl. Polym. Sci.* 55(11), 1573-1581. DOI: 10.1002/app.1995.070551108

Homma, H., Kubo, S., Yamada, T., Matsushita, Y., and Uraki, Y. (2008). "Preparation and characterization of amphiphilic lignin derivatives as surfactants," *Journal of Wood Chemistry and Technology* 28(4), 270-282. DOI: 10.1080/02773810802510688

Hoshino, E., Chiwaki, M., Suzuki, A., and Murata, M. (2000). "Improvement of cotton cloth soil removal by inclusion of alkaline cellulase from *Bacillus* sp KSM-635 in detergents," *J. Surfact. Deterg.* 3(3), 317-326. DOI: 10.1007/s11743-000-0135-y

Hubbe, M. A. (1984). "Theory of detachment of colloidal particles from flat surfaces exposed to flow," *Colloids Surf* 12(1-2), 151-178. DOI: 10.1016/0166-6622(84)80096-7

Hubbe, M. A. (1985). "Detachment of colloidal hydrous oxide spheres from flat solids exposed to flow. 2. Mechanism of release," *Colloids Surf.* 16(3-4), 249-270. DOI: 10.1016/0166-6622(85)80257-2

Hubbe, M. A. (1987). "Detachment of colloidal hydrous oxide spheres from flat solids exposed to flow. 3. Forces of adhesion," *Colloids Surf.* 25(2-4), 311-324. DOI: 10.1016/0166-6622(87)80311-6

Hubbe, M. A. (2006). "Bonding between cellulosic fibers in the absence and presence of dry-strength agents – A review," *BioResources* 1(2), 281-318. DOI: 10.15376/biores.1.2.281-318

Hubbe, M. A., Gardner, D. J., and Shen, W. (2015). "Contact angles and wettability of cellulosic surfaces: A review of proposed mechanisms and test strategies," *BioResources* 10(4), 8657-8749. DOI: 10.15376/biores.10.4.Hubbe_Gardner_Shen

Hubbe, M. A., Hasan, S. H., and Ducoste, J. J. (2011). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals," *BioResources* 6(2), 2161-2287. DOI: 10.15376/biores.6.2.2161-2287

Hubbe, M. A., McLean, D. S., Stack, K. R., Lu, X. M., Strand, A., and Sundberg, A. (2020). "Self-assembly of alkyl chains of fatty acids in papermaking systems: A review of related pitch issues, hydrophobic sizing, and pH effects," *BioResources* 15(2), 4591-4635. DOI: 10.15376/biores.15.2.4591-4635

Hubbe, M. A., and Rojas, O. J. (2008). "Colloidal stability and aggregation of lignocellulosic materials in aqueous suspension: A review," *BioResources* 3(4), 1419-1491. DOI: 10.15376/biores.3.4.1419-1491

Hubbe, M. A., Sundberg, A., Mocchiutti, P., Ni, Y., and Pelton, R. (2012). "Dissolved and colloidal substances (DCS) and the charge demand of papermaking process waters and suspensions: A review," *BioResources* 7(4), 6109-6193. DOI: 10.15376/biores.7.4.6109-6193

Huggins, J. H., and Langguth, R. P. (1968). "Laboratory studies of detergency and soil redeposition properties of polyester/cotton," *Soap Chem. Specialties* 44(7), 70.

Hurem, Z., Vucelic, D., and Hajman, D. (1992). "Determination of zeolite contents deposits on textiles during washing," *Spectrosc. Let.* 25(7), 901-909. DOI: 10.1080/00387019208018203

Isaka, A., Ohashi, T., Koizumi, F., Fujiwara, E., Ando, S., and Kuzuhara, A. (2021). "Direct quantitative analysis on detergency of soil components using ATR-FT/IR," *J. Fiber Sci. Technol.* 77(6), 174-181. DOI10.2115/fiberst.2021-0017

Iyer, P. V., and Ananthanarayan, L. (2008). "Enzyme stability and stabilization – Aqueous and non-aqueous environment," *Process Biochem.* 43(10), 1019-1032. DOI: 10.1016/j.procbio.2008.06.004

Jadhav, J. v., Anbu, P., Yadav, S., Pratap, A. P., and Kale, S. B. (2019). "Sunflower acid oil-based production of rhamnolipid using *Pseudomonas aeruginosa* and its application in liquid detergents," *Journal of Surfactants and Detergents* 22(3), 463-476. DOI: 10.1002/jsde.12255

Jardim, J. M., Hart, P. W., Lucia, L., and Jameel, H. (2020). "Insights into the potential of hardwood kraft lignin to be a green platform material for emergence of the biorefinery," *Polymers* 12(8), article no. 1795. DOI: 10.3390/POLYM12081795

Jain, A. (2017). "Alternative to water based fabric cleaner in textile and detergent processes," *Adv. Mater. Sci. Eng.* 2017, article no. 3736175. DOI: 10.1155/2017/3736175

Jeoh, T., Ishizawa, C. I., Davis, M. F., Himmel, M. E., Adney, W. S., and Johnson, D. K. (2007). "Cellulase digestibility of pretreated biomass is limited by cellulose accessibility," *Biotech. Bioeng.* 98(1), 112-122. DOI: 10.1002/bit.21408

Kaewpukpa, R., Chavadej, S., and Scamehorn, J. F. (2008). "Oily soil detergency under microemulsion conditions: Effects of oil loading and surfactant adsorption," in: *Smart Materials*, T. Tunkasiri (ed.), book series *Materials Research* 55-57, article no. 929. DOI: 10.4028/www.scientific.net/AMR.55-57.929

Kalak, T., and Cierpiszewski, R. (2015). "Correlation analysis between particulate soil removal and surface properties of laundry detergent solutions," *Textile Res. J.* 85(18), 1884-1906. DOI: 10.1177/0040517515578329

Kanicky, J. R., and Shah, D. O. (2002). "Effect of degree, type, and position of unsaturation on the p*K*a of long-chain fatty acids," *J. Colloid Interface Sci.* 256(1), 201-207. DOI: 10.1006/jcis.2001.8009

Karthick, R. A., Jangir, K., and Chattopadhyay, P. (2018). "Foaming and cleaning performance comparison of liquid detergent formulations using mixtures of anionic and nonionic surfactants," *Tenside Surfact. Deterg.* 55(2), 162-168. DOI: 10.3139/113.110553

Kawase, T., Enishi, H., Fujii, T., and Minagawa, M. (1994). "Removal of fatty acid by solubilization into micelles of nonionic surfactants," *J. Jpn. Oil Chem. Soc.* 43, 124-130. DOI: 10.5650/jos1956.43.124

Kawase, T., Yamada, K., Fujii, T., and Minagawa, M. (1991). "Removal of fatty acid by sodium dodecyl sulfate solution removal mechanism by solubilization," *J. Jpn. Oil Chem. Soc.* 40, 126-132. DOI: 10.5650/jos1956.40.126

Kert, M., and Simoncić, B. (2008). "Efficiency of liquid detergent at removing standard soil from cotton fabric," ITC&DC: 4th International Textile Clothing & Design Conference, Book of Proceedings, Z. Dragcevic (ed.), Dubrovnik, Croatia, pp. 382-387.

Kim, S. (2008). *Science of Detergent and Washing*, 2nd Ed., Kyomunsa, Paju, pp. 352.

Kiriyama, T., Sugiura, H., and Uehara, M. (2003). "Residual washing detergent in cotton clothes: A factor of winter deterioration of dry skin in atopic dermatitis," *J. Dermatol.* 30(10), 708-712. DOI10.1111/j.1346-8138.2003.tb00463.x

Kissa, E. (1981). "Wetting and detergency," *Pure Appl. Chem*. 53(11), 2255-2268. DOI: 10.1351/pac198153112255

Kissa, E. (1987). "Kinetics and mechanisms of soiling detergency," in: *Detergency: Theory and Technology*, W. Gale Cutler and Erik Kissa (eds.), *Surfactant Science Series* 20, Dekker, Ch. 4, pp. 193-331. DOI: 10.1201/9781003065494-4

Kokol, V., Vivod, V., Arnus, S., Cernigoj, U., Galicic, B., Vazner, K. O., Neral, B., and Mihelic, A. (2018). "Zeolite integrated nanocellulose films for removal of loose anionic reactive dye by adsorption vs. filtration mode during textile laundering," *Fibers Polym.* 19(7), 1556-1566. DOI: 10.1007/s12221-018-8036-z

Komaki, M., Kim, S. K., and Hashimoto, T. (2002). "Fatty acid soil detergency performance of poly(sodium alpha-hydroxyacrylate)," *J. Surfact. Deterg.* 5(1), 25-31. DOI: 10.1007/s11743-002-0201-5

Kontturi, E., Suchy, M., Penttila, P., Jean, B., Pirkkalainen, K., Torkkeli, M., and Serimaa, R. (2011). "Amorphous characteristics of an ultrathin cellulose film," *Biomacromol.* 12(3), 770-777. DOI: 10.1021/bm101382q

Koteich Khatib, S., Bullón, J., Vivas, J., Bahsas, A., Rosales-Oballos, Y., Marquez, R., Forgiarini, A., and Salager, J. L. (2020). "Synthesis, characterization, evaluation of interfacial properties and antibacterial activities of dicarboxylate anacardic acid derivatives from cashew nut shell liquid of *Anacardium occidentale* L.," *Journal of Surfactants and Detergents* 23(3), 503-512. DOI: 10.1002/jsde.12384

Kruschwitz, A., Augsburg, A., and Stamminger, R. (2013). "How effective are alternative ways of laundry washing?" *Tenside Surfactants Detergents* 50(4), 263-269. DOI: 10.3139/113.110258

Lambert, J. M. (1950). "Some physical-chemical aspects of cotton detergency – Cationic adsorption and exchange as shown by radiocalcium tracer studies," *Indus. Eng. Chem.* 42(7), 1394-1398. DOI10.1021/ie50487a038

Lavoine, N., Desloges, I., Dufresne, A., and Bras, J. (2012). "Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review," *Carbohyd. Polym.* 90(2), 735-764. DOI: 10.1016/j.carbpol.2012.05.026

Leal, J. S., Perez, L., Ribosa, I., Garcia, M. T., and Gonzalez, J. J. (1996). "Comparative study of conventional and compact detergents," *J. Amer. Oil Chemists Soc.* 73(1), 27-30. DOI: 10.1007/BF02523444

Lee, A., Seo, M. H., Yang, S., Koh, J., and Kim, H. (2008). "The effects of mechanical actions on washing efficiency," *Fiber Polym.* 9(1), 101-106. DOI: 10.1007/s12221-008-0017-1

Lee, S., Akeprathumchai, S., Bundidamorn, D., Salaipeth, L., Poomputsa, K., Ratanakhanokchai, K., Chang, K. L., and Phitsuwan, P. (2021). "Interplays of enzyme, substrate, and surfactant on hydrolysis of native lignocellulosic biomass," *Bioengineered* 12(1), 5110-5124. DOI: 10.1080/21655979.2021.1961662

Levinson, M. I. (1999). "Rinse-added fabric softener technology at the close of the twentieth century," *J. Surfact. Deterg.* 2(2), 223-235. DOI: 10.1007/s11743-999-0077-4

Li, T., and Takkellapati, S. (2018). "The current and emerging sources of technical lignins and their applications," *Biofuels, Bioproducts and Biorefining* 12(5), 756-787. DOI: 10.1002/bbb.1913

Li, Y. H., and Hardin, I. R. (1998). "Enzymatic scouring of cotton – Surfactants, agitation, and selection of enzymes," *Textile Chem. Colorist* 30(9), 23-29.

Li, Y. Q., Liu, J. Q., and Qian, C. J. (2012). "Effect of laundering by detergent containing bleaches on cotton fabric," in: *Equipment Manufacturing Technology*, J. T. Han, S. H. Jiao, and Z. Y. Jiang (eds.), Vol. 422, pp. 657-662. DOI: 10.4028/www.scientific.net/AMR.422.657

Lindström, T. (2017). "Aspects on nanofibrillated cellulose (NFC) processing, rheology and NFC-film properties," *Current Opin. Colloid Inter. Sci.* 29, 68-75. DOI: 10.1016/j.cocis.2017.02.005

Liu, Y. S., Baker, J. O., Zeng, Y. N., Himmel, M. E., Haas, T., and Ding, S. Y. (2011). "Cellobiohydrolase hydrolyzes crystalline cellulose on hydrophobic faces," *Biolog. Chem.* 286(13), 11195-11201. DOI: 10.1074/jbc.M110.216556

Lohman, J. H. (2002). "A history of dry cleaners and sources of solvent releases from dry cleaning equipment," *Environ. Forensics* 3(1), 35-58. DOI: 10.1006/enfo.2002.0079

Lou, H. M., Zeng, M. J., and Pang, Y. X. (2018). "Nonionic surfactants enhanced enzymatic hydrolysis of cellulose by reducing cellulase deactivation caused by shear force and air-liquid interface," *Bioreour. Technol.* 249, 1-8. DOI: 10.1016/j.biortech.2017.07.066

Lu, C., Rosencrance, S., Swales, D., Covarrubias, R., and Hubbe, M. A. (2020). "Dry strength: Strategies for stronger paper," in: *Make Paper Products Stand Out. Strategic Use of Wet End Chemical Additives*, M. A. Hubbe and S. Rosencrance, S. (eds.) TAPPI Press, Atlanta, GA, Ch. 7, pp. 155-196.

Luxbacher, T., Pusic, T., and Petrinic, I. (2008). "Monitoring the washing efficiency of stained cotton fabrics by streaming potential measurement," 4th International Textile Clothing & Design Conference, Book of Proceedings, Z. Dragcevic (ed.), p. 825.

Mahe, M., Vignes-Adler, M., Rousseau, A., Jacquin, C. G., and Adler, P. M. (1988). "Adhesion of droplets on a solid wall and detachment by a shear flow: I. Pure systems," *J. Colloid Interface Sci.* 126(1), 314-328. DOI: 10.1016/0021-9797(88)90125-7

Mansour, H. M., and Zografi, G. (2007). "Relationships between equilibrium spreading pressure and phase equilibria of phospholipid bilayers and monolayers at the air-water interface," *Langmuir* 23(7), 3809-3819. DOI: 10.1021/la063053o

Matheson, K. L. (1996). "Formulation of household and industrial detergents," in: *Soaps and Detergents: A Theoretical and Practical Review*, L. Spitz (ed.), AOCS Press, Champaign, IL, Ch. 11, pp. 314-332.

Matsusaka, S., Maruyama, H., Matsuyama, T., and Ghadiri, M. (2010). "Triboelectric charging of powders: A review," *Chem. Eng. Sci.* 65(2), 5781-5807. DOI: 10.1016/j.ces.2010.07.005

Mazurek, K. A., Rajaratnam, N., and Sego, D. C. (2001). "Scour of cohesive soil by submerged circular turbulent impinging jets," *J. Hydraulic Eng. – ASCE* 127(7), 598-606. DOI: 10.1061/(ASCE)0733-9429(2001)127:7(598)

McBain, J. W., Humphreys, C. W., and Kawakami, Y. (1929). "The rates of saponification of various commercial oils, fats, and waxes and pure triglycerides by aqueous alkali," *J. Chem. Soc.* 1929, 2185-2197. DOI: 10.1039/jr9290002185

Mercantili, L., Davis, F., and Higson, S. P. J. (2014). "Ultrasonic initiation of the alkaline hydrolysis of triglycerides (saponification) without phase catalysis," *J. Surfact. Deterg.* 17(1), 133-141. DOI: 10.1007/s11743-013-1450-8

Miller, C. A., and Raney, K. H. (1993). "Solubilization emulsification mechanisms of detergency," *Colloids Surf. A – Physicochem. Eng. Aspects* 74(2-3), 169-215. DOI: 10.1016/0927-7757(93)80263-E

Milojević, V. S., Nikolić, L. B., Nikolić, G., and Stamenković, J. (2013). “The influence of sodium-polyacrylic macromolecular chain length to the powder detergents secondary washing performances,” *Industrija* 67(1), 35-40. DOI: 10.2298/HEMIND120220040M

Miñana-Perez, M., Graciaa, A., Lachaise, J., and Salager, J. L. (1995). “Solubilization of polar oils with extended surfactants,” *Colloids Surf. A* 100, 217-224. DOI: 10.1016/0927-7757(95)03186-H

Moller, J. V., and Lemaire, M. (1993). “Detergent binding as a measure of hydrophobic surface-area of integral membrane-proteins,” *J. Biol. Chem.* 268(25), 18659-18672. DOI: 10.1016/S0021-9258(17)46681-6

Moskaliuk, K., and Katović, D. (1997). “Impact of the usage of sodium hypochlorite in textile bleaching upon water pollution,” *Tekstil* 46(3), 139-144.

Muir, A. C., McKeown, P., Li, Y., Kobine, J. J., and Bird, M. R. (2013). “The removal of food fat based soils during the washing of fabrics,” *Chem. Eng. Res. Design* 91(9), 1602-1613. DOI10.1016/j.cherd.2013.03.004

Muller, M., Grosse, I., Jacobasch, H. J., and Sams, P. (1998). “Surfactant adsorption and water desorption on thin cellulose films monitored by in-situ ATR FTIR spectroscopy,” *Tenside Surfact. Deterg.* 35(5), 354-359.

Murata, M., Hoshino, E., Yokosuka, M., and Suzuki, A. (1991). “New detergent mechanism with use of novel alkaline cellulase,” *J. Amer. Oil Chem. Soc.* 68(7), 553-558. DOI: 10.1007/BF02663833

Murata, M., Hoshino, E., Yokosuka, M., and Suzuki, A. (1993). “New detergent mechanism using cellulase revealed by change in physicochemical properties of cellulose,” *J. Amer. Oil Chem. Soc.* 70(1), 53-58. DOI: 10.1007/BF02545367

Murphy, D. S. (2015). “Fabric softener technology: A review,” *J. Surfact. Deterg.* 18(2), 199-204. DOI: 10.1007/s11743-014-1658-2

Nakama, Y. (2017). “Surfactants,” in: *Cosmetic Science and Technology: Theoretical Principles and Applications*, K. Sakamoto, R. Y. Lockhead, H. I. Maibach, and U. Yamashita (eds.), Elsevier, Amsterdam, Ch. 15, pp. 231-244. DOI: 10.1016/B978-0-12-802005-0.00015-X

Napper, D. H. (1977). “Steric stabilization,” *J. Colloid Interface Sci.* 58(2), 390-407. DOI: 10.1016/0021-9797(77)90150-3

Nishiyama, Y., Kim, U. J., Kim, D. Y., Katsumata, K. S., May, R. P., and Langan, P. (2003). “Periodic disorder along ramie cellulose microfibrils,” *Biomacromol.* 4(4), 1013-1017. DOI: 10.1021/bm025772x

Oakes, J. (2005). “Formulation of colour-care and heavy duty detergents: A review,” *Coloration Technol.* 121(1), 1-6. DOI: 10.1111/j.1478-4408.2005.tb00239.x

Obendorf, S. K. (2000). “Detergency of used motor oil from textiles” (reprinted from *Journal of Surfactants and Detergents*),” *Chimica Oggi-Chemistry Today* 18(11-12), 77-79.

Obendorf, S. K. (2004). “Microscopy to define soil, fabric and detergent formulation characteristics that affect detergency: A review,” *AATCC Rev.* 4(1), 17-23.

O'Connell, D. W., Birkinshaw, C., and O'Dwyer, T. F. (2008). “Heavy metal adsorbents prepared from the modification of cellulose: A review,” *Bioresour. Technol.* 99(15), 6709-6724. DOI: 10.1016/j.biortech.2008.01.036

Olsen, H. S., and Falholt, P. (1998). “The role of enzymes in modern detergency,” *Journal of Surfactants and Detergents* 1(4), 555-567. DOI: 10.1007/s11743-998-0058-7

Olsson, A. M., and Salmén, L. (2004). "The softening behavior of hemicelluloses related to moisture," in: *Hemicelluloses: Science and Technology*, P. Gatenholm (ed.), *ACS Symp. Ser.* 864, 184-197. DOI: 10.1021/bk-2004-0864.ch013

Ooshima, H., Sakata, M., and Harano, Y. (1986). "Enhancement of enzymatic hydrolysis of cellulose by surfactant," *Biotechnol. Bioeng.* 28(11), 1727-1734. DOI: 10.1002/bit.260281117

Ortiz, M. S., Alvarado, J. G., Zambrano, F., and Marquez, R. (2022). "Surfactants produced from carbohydrate derivatives: A review of the biobased building blocks used in their synthesis," *Journal of Surfactants and Detergents* 25(2), 147-183. DOI: 10.1002/jsde.12581

Ou, J. H., Kong, Z. X., Yang, R., and Dai, Z. L. (2021). "Synthesis of a lignin-based alcohol ether carboxylate surfactant and its application as cotton fiber detergent," *J. Dispersion Sci. Technol.* Early access. DOI: 10.1080/01932691.2021.1956323

Ou, J. H., and Zhao, J. H. (2017). "Modification of sodium lignosulfonate and evaluation of its potential use as detergent builders," *J. Wood Chem. Technol.* 37(2), 99-109. DOI: 10.1080/02773813.2016.1235589

Paria, S., and Khilar, K. C. (2004). "A review on experimental studies of surfactant adsorption at the hydrophilic solid-water interface," *Advan. Colloid Interface Sci.* 110(3), 75-95. DOI: 10.1016/j.cis.2004.03.001

Paria, S., Manohar, C., and Khilar, K. C. (2004). "Effect of cationic surfactant on the adsorption characteristics of anionic surfactant on cellulose surface," *Colloids Surf. A.: Phyicochem. Eng. Aspects* 232, 139-142. DOI: 10.1016/j.colsurfa.2003.10.016

Paria, S., Manohar, C., and Khilar, K. C. (2005a). "Adsorption of anionic and non-ionic surfactants on a cellulosic surface," *Colloids Surf. A.: Phyicochem. Eng. Aspects* 252, 221-229. DOI: 10.1016/j.colsurfa.2004.09.022

Paria, S., Manohar, C., and Khilar, K. C. (2005b). "Kinetics of adsorption of anionic, cationic, and nonionic surfactants," *Ind. Eng. Chem. Res.* 44(9), 3091-3098. DOI: 10.1021/ie049471a

Paul, T., Das, A., Mandal, A., Halder, S. K., Jana, A., Malty, C., DasMohapatra, P. K., Pati, B. R., and Mondal, K. C. (2014). "An efficient cloth cleaning properties of a crude keratinase combined with detergent: Towards industrial viewpoint," *J. Cleaner Prod.* 66, 672-684. DOI: 10.1016/j.jclepro.2013.10.054

Pawlak, J. J., Frazier, R., Vera, R. E., Wang, Y., and Gonzalez, R. (2022). "The softness of hygiene tissue," *BioResources* 17(2), 3509-3550. DOI: 15376/biores.17.2.Pawlak

Pei, Z. J., and Ferreira, P. M. (1998). "Modeling of ductile-mode material removal in rotary ultrasonic machining," *Int. J. Machine Toos Manuf.* 38(10-11), 1399-1418. DOI: 10.1016/S0890-6955(98)00007-8

Peila, R., Grande, G. A., Giansetti, M., Rehrnan, S., Sicardi, S., and Rovero, G. (2015). "Washing off intensification of cotton and wool fabrics by ultrasounds," *Ultrasonics Sonochem.* 23, 324-332. DOI: 10.1016/j.ultsonch.2014.09.004

Penfold, J., Tucker, I., Petkov, J., and Thomas, R. K. (2007). "Surfactant adsorption onto cellulose surfaces," *Langmuir* 23(16), 8357-8364. DOI: 10.1021/la700948k

Phan, T. T., Witthayapanyanon, A., Harwell, J. H., and Sabatini, D. A. (2010). "Microemulsion-based vegetable oil detergency using an extended surfactant," *Journal of Surfactants and Detergents* 13, 313-319. DOI:10.1007/s11743-010-1184-9

Phaodee, P., Adamy, S. T., Zehr, R. T., Harwell, J. H., and Grady, B. P. (2021). "Improved cold-water detergency of malodorous soil correlating with hydrophilic-lipophilic deviation concept," *J. Surfactants Detergents* 25(2), 265-273. DOI: 10.1002/jsde.12561

Phaodee, P., Attaphong, C., and Sabatini, D. A. (2019). "Cold water detergency of triacylglycerol semisolid soils: The effect of salinity, alcohol type, and surfactant systems," *Journal of Surfactants and Detergents* 22(5), 1175-1187. DOI: 10.1002/jsde.12234

Phaodee, P., Harwell, J. H., and Sabatini, D. A. (2020). "Correlation between detergency of different oily and solid non-particulate soils and hydrophilic-lipophilic deviation," *J. Surfactants Detergents* 23(5), 953-962. DOI: 10.1002/jsde.12441

Phillips, D., Taylor, J., Lakhanpal, R., Scotney, T., and Bevan, G. (2001). "Comparison of the performance of zeolite-containing and phosphate-containing ECE reference detergents in three different wash fastness tests," *Coloration Technol.* 117(1), 6-12. DOI: 10.1111/j.1478-4408.2001.tb00328.x

Pinto, I. S. S., Neto, I. F. F., and Soares, H. M. V. M. (2014). "Biodegradable chelating agents for industrial, domestic, and agricultural applications – A review," *Environ. Sci. Pollut. Res.* 21(20), 11893-11906. DOI: 10.1007/s11356-014-2592-6

Poffenberger, C., Deae, Y., and Zeman, W. (2000). "Novel hydrophilic softeners for tissue and towel applications," *Proc. TAPPI 2000 Papermakers Conf.*, TAPPI Press, Atlanta, pp. 85-93.

Ponnusamy, T., Dubal, S. A., and Momin, S. A. (2008). "Studies in detergency: Influence of different factors for removing motor oil stain from the cotton fabric," *J. Dispersion Sci. Technol.* 29(8), 1123-1128. DOI: 10.1080/01932690701817842

Powe, W. C. (1963). "Removal of fatty soils from cotton in aqueous detergent systems," *J. Amer. Oil Chemists Soc.* 40(7), 290-294. DOI: 10.1007/BF02633695

Powney, J., and Wood, L. J. (1940a). "The properties of detergent solutions - Part IX. - The electrophoretic mobility of oil drops in detergent solutions," *Trans Faraday Soc.* 35(3), 57-62. DOI: 10.1039/tf9403500057

Powney, J., and Wood, L. J. (1940b). "The properties of detergent solutions. Part X. Some further observations on electrophoretic mobilities in detergent solutions," *Trans. Faraday Soc.* 35(3), 420-425. DOI: 10.1039/tf9403500420

Pratap, A., Wadekar, S., Kale, S., Lali, A., and Bhowmick, D. N. (2011). "Non-traditional oils as newer feedstock for rhamnolipids production by *Pseudomonas aeruginosa* (ATCC 10145)," *JAOCS, Journal of the American Oil Chemists' Society* 88(12), 1935-1943. DOI: 10.1007/S11746-011-1875-Z

Pucha, R. (1984). "Cationic surfactants in laundry detergents and laundry aftertreatment aids," *J. Amer. Oil Chemists Soc.* 61(2), 367-376. DOI: 10.1007/BF02678796

Pučić, M. (2008). "Washing technology Spirit Pro Line of Swiss company Schulthess for semi-professional companies," *Tekstill* 57, 550-552.

Pugh, R. J. (1996). "Foaming, foam films, antifoaming and defoaming," *Adv. Colloid Interface Sci.* 64, 67-142. DOI: 10.1016/0001-8686(95)00280-4

Pukale, D. D., Bansode, A. S., Pinjari, D. V., Kulkarni, R. R., and Sayed, U. (2017). "Application of silicone surfactant along with hydrocarbon surfactants to textile washing for the removal of different complex stains," *Surfactants Detergents* 20(1), 287-295. DOI: 10.1007/s11743-016-1901-0

Pusić, T., Soljacić, I., Pezelj, E., Koricić, M., and Madarević, D. (2008). "The modifications of cotton and polycotton fabrics during frequent laundering," ITC&DC: 4th International Textile Clothing & Design Conference, Book of Proceedings, Z. Dragcevic (ed.), p. 441.

Pusić, T., Sostar-Turk, S., Soljacić, I., Tarbuk, A., Fijan, R., and Arnus, S. (2006). “Primary washing effect of powder and liquid detergents,” *Tekstil* 55(1), 11-18.

Rahman, M. S., Hasan, M. S., Nitai, A. S., Nam, S., Karmakar, A. K., Ahsan, M. S., Shiddiky, M. J. A., and Ahmed, M. B. (2021). “Recent developments of carboxymethyl cellulose,” *Polymers* 13(8), article no. 1345. DOI: 10.3390/polym13081345

Raney, K., and Miller, C. A. (1987). “Defoaming effect of calcium soap,” *J. Colloid Interface Sci.* 119(2), 539-547. DOI10.1016/j.jcis.2004.06.103

Raney, K., Benton, W., and Miller, C. A. (1987). “Optimum detergency conditions with nonionic surfactants. 1. Ternary water surfactant hydrocarbon systems,” *J. Colloid Interface Sci.* 117, 282-290. DOI: 10.1016/0021-9797(87)90192-5

Rathinamoorthy, R., and Raja Balasaraswathi, S. (2020). “A review of the current status of microfiber pollution research in textiles,” *International Journal of Clothing Science and Technology* 33(3), 364-387. DOI: 10.1108/ijcst-04-2020-0051

Ren, J., Shao, J. Z., Yu, M. L., Xu, C. Y., and Qiu, Y. Q. (2012). “Fluorescence analysis of detergency mechanisms of olive oil on single cotton fibers,” in: *Eco-dyeing, Finishing and Green Chemistry,* J. H. Shao and Q. G. Fan (eds.), series: *Advanced Materials Research* 441, 691-694. DOI: 10.4028/www.scientific.net/AMR.441.691

Rhee, H., Young, R. A., and Sarmadi, A. M. (1993a). “The effect of functional finishes and laundering on textile materials. 1. Surface characteristics,” *J. Textile Inst.* 84(3), 394-405. DOI: 10.1080/00405009308658972

Rhee, H., Young, R. A., and Sarmadi, A. M. (1993b). “The effect of functional finishes and laundering on textile materials. 2. Characterization of liquid flow,” *J. Textile Inst.* 84(3), 406-418. DOI: 10.1080/00405009308658973

Rijavec, T., Jevšnik, S., Solijačić, I., Tomljenović, A., Višić, K., and Pušić, T. (2015). “Physical and chemical effects of washing and wet cleaning on durable press finished cotton fabrics,” *Textile Res. J.* 85(6), 632-645. DOI: 10.1177/0040517514547212

Rojvoranun, S., Chadavipoo, C., Pengjun, W., Chavadej, S., Scamehorn, J. F., and Sabatini, D, A, (2012a). “Mechanistic studies of particulate soil detergency: I. Hydrophobic soil removal,” *J. Surfactants Detergents* 15(3), 277-289. DOI: 10.1007/s11743-011-1319-7

Rojvoranun, S., Chavadej, S., Scamehorn, J. F., and Sabatini, D. A. (2012b). “Mechanistic studies of particulate soil detergency: II: Hydrophilic soil removal,” *J. Surfactants Detergents* 15(6), 663-677. DOI: 10.1007/s11743-012-1362-z

Rosen, M. J., and Murphy, D. S. (1986). “Synergism in binary-mixtures of surfactants. 5. 2-phase liquid liquid-systems at low surfactant concentrations,” *J. Colloid Interface Sci.* 110(1), 224-236. DOI: 10.1016/0021-9797(86)90371-1

Rueda, C., Calvo, P. A., Moncalian, G., Ruiz, G., and Coz, A. (2015). “Biorefinery options to valorize the spent liquor from sulfite pulping,” *J. Chem. Technol. Biotech.* 90(12), 2218-2226. DOI: 10.1002/jctb.4536

Salager, J.-L., Antón, R., Sabatini, D. A., Harwell, J. H., Acosta, E. J., and Tolosa, L. I. (2005). “Enhancing solubilization in microemulsions – State of the art and current trends,” *J. Surfactants Detergents* 8, 3-21. DOI: 10.1007/s11743-005-0328-4

Salager, J.-L., Forgiarini, A. M., and Bullón, J. (2013). “How to attain ultralow interfacial tension and three-phase behavior with surfactant formulation for enhanced oil recovery: A Review. Part 1. Optimum formulation for simple surfactant–oil–water ternary systems,” *J. Surfact. Deterg.* 16, 449-472. DOI: 10.1007/s11743-013-1470-4

Salager, J.-L., Forgiarini, A., and Marquez, R. (2019). "Extended surfactants including an alkoxylated central part intermediate producing a gradual polarity transition—A review of the properties used in applications such as enhanced oil recovery and polar oil solubilization in microemulsions," *Journal of Surfactants and Detergents* 22(5), 935-972. DOI: 10.1002/jsde.12331

Salager, J.-L., Forgiarini, A. M., and Rondón, M. J. (2017). "How to attain ultralow interfacial tension and three-phase behavior with a surfactant formulation for enhanced oil recovery: A Review—Part 3. Practical procedures to optimize the laboratory research according to the current state of the art in surfactant mixing," *J. Surfact. Deterg.* 20, 3-19 (2017). DOI: 10.1007/s11743-016-1883-y

Salager, J.-L., Graciaa, A., and Lachaise, J. (1998). "Improving solubilization in microemulsions with additives. Part III: Lipophilic linker optimization," *J. Surfactants Detergents* 1(3), 403-406. DOI: 10.1007/s11743-998-0043-1

Salager, J.-L., Marquez, R., Bullon, J., and Forgiarini, A. (2022). "Formulation in surfactant systems: From Winsor to HLD_N," *Encyclopedia* 2(2), 778-839. DOI: 10.3390/encyclopedia2020054

Salager, J.-L., Morgan, J. C., Schechter, R. S., Wade, W. H., and Vasquez, E. (1979). "Optimum formulation of surfactant/water/oil systems for minimum interfacial tension or phase behavior," *Society of Petroleum Engineers Journal* 19, 107-115. DOI: 10.2118/7054-PA

Saleeb, F. Z. (1970). "Adsorption of surface active agents at solid-liquid interface. 1. Adsorption of Aerosol-OT," *Z. Phys. Chem. Leipzig* 244(1-2), 85. DOI: 10.1515/zpch-1970-24406

Salmén, L., Back, E., and Alwarsdotter, Y. (1984). "Effects of on-aqueous plasticizers on the thermal softening of paper," *J. Wood Chem. Technol.* 4(3), 347-365. DOI: 10.1080/02773818408070654

Samanta, A. K., Mitra, S., Singhee, D., and Parekh, S. (2004). "Efficacy of selective surfactants/detergents as washing agents on soiled white and dyed cotton fabrics," *Indian J. Fibre Textile Res.* 29(2), 223-232.

Sanders, H. L., and Lambert, J. M. (1950). "An approach to a more realistic cotton detergency test," *J. Amer. Oil Chemists Soc.* 27(5), 153-159. DOI: 10.1007/BF02634409

Santos, D. K. F., Rufino, R. D., Luna, J. M., Santos, V. A., and Sarubbo, L. A. (2016). "Biosurfactants: Multifunctional Biomolecules of the 21st Century," *International Journal of Molecular Sciences* 17(3). DOI: 10.3390/IJMS17030401

Saxena, R. K., Saran, S., Isar, J., and Kaushik, R. (2017). "Production and applications of succinic acid," *Current Developments in Biotechnology and Bioengineering: Production, Isolation and Purification of Industrial Products* 601-630. DOI: 10.1016/B978-0-444-63662-1.00027-0

Sayyed, A. J., Deshmukh, N. A., and Pinjari, D. V. (2019). "A critical review of manufacturing processes used in regenerated cellulosic fibres: Viscose, cellulose acetate, cuprammonium, LiCl/DMAc, ionic liquids, and NMMO based lyocell," *Cellulose* 26(5), 2913-2940. DOI: 10.1007/s10570-019-02318-y

Schaffer, J. F., and Woodhams, R. T. (1977). "Polyelectrolyte builders as detergent phosphate replacements," *Indust. Eng. Chem. Prod. Res. Devel.* 16(1), 3-11. DOI: 10.1021/i360061a002

Scheibel, J. J. (2004). “The evolution of anionic surfactant technology to meet the requirements of the laundry detergent industry,” *Journal of Surfactants and Detergents* 7(4), 319-328. DOI: 10.1007/s11743-004-0317-7

Scheuing, D. R., and Hsieh, J. C. L. (1988). “Detergency of nonionic surfactants toward a solid hydrocarbon soil studied by FT-IR,” *Langmuir* 4(6), 1277-1283. DOI: 10.1021/la00084a012

Schmidt, L. M., Mthembu, L. D., Reddy, P., Deenadayalu, N., Kaltschmitt, M., and Smirnova, I. (2017). “Levulinic acid production integrated into a sugarcane bagasse based biorefinery using thermal-enzymatic pretreatment,” *Industrial Crops and Products* 99, 172-178. DOI: 10.1016/j.indcrop.2017.02.010

Schmitz, A., and Stamminger, R. (2014). “Usage behaviour and related energy consumption of european consumers for washing and drying,” *Energy Efficiency* 7, 937-954. DOI: 10.1007/s12053-014-9268-4

Schmutz, A., Jenny, T., and Ryser, U. (1994). “A caffeoyl fatty acid glycerol ester from wax associated with green cotton fiber suberin,” *Phytochem.* 36(6), 1343-1346. DOI: 10.1016/S0031-9422(00)89721-6

Schott, H. (1967). “Interaction of anionic detergents with cellulose,” *Textile Res. J.* 37(4), 336-336. DOI: 10.1177/004051756703700412

Schott, H. (1969). “Comments regarding washability of cotton and rolling-up mechanism of detergency,” *Textile Res. J.* 39(3), 296-298. DOI: 10.1177/004051756903900318

Schwuger, M. J., and Smulders, E. J. (1987). “Inorganic builders,” in: *Detergency: Theory and Technology*, W. Gale Cutler and Erik Kissa (eds.), *Surfactant Science Series* 20, Dekker, Ch. 6, pp. 371-439. DOI: 10.1201/9781003065494-6

Seo, D. J., Fujita, H., and Sakoda, A. (2011). “Effects of a non-ionic surfactant, Tween 20, on adsorption/desorption of saccharification enzymes onto/from lignocelluloses and saccharification rate,” *Adsorption – J. Int. Adsorp. Soc.* 17(5), 813-822. DOI: 10.1007/s10450-011-9340-8

Sharma, R., Chisti, Y., and Banerjee, U. C. (2001). “Production, purification, characterization, and applications of lipases,” *Biotech. Adv.* 19(8), 627-662. DOI: 10.1016/S0734-9750(01)00086-6

Shen, Y. H. (2002). “Estimation of surface area of montmorillonite by ethylene oxide chain adsorption,” *Chemosphere* 48(10), 1075-1079. DOI: 10.1016/S0045-6535(02)00200-X

Shibafuji, Y., Nakamura, A., Uchihashi, T., Sugimoto, N., Fukuda, S., Watanabe, H., Samejima, M., Ando, T., Noji, H., Koivula, A., Igarashi, K., and Iino, R. (2014). “Single-molecule imaging analysis of elementary reaction steps of *Trichoderma reesei* cellobiohydrolase I (Cel7A) hydrolyzing crystalline cellulose I (alpha) and III (I),” *J. Biolog. Chem.* 289(20), 14056-14065. DOI: 10.1074/jbc.M113.546085

Shin, S., Warren, P. B., and Stone, H. A. (2018). “Cleaning by surfactant gradients: Particulate removal from porous materials and the significance of rinsing in laundry detergency,” *Physical Review Applied* 9(3), article no. 034012. DOI: 10.1103/PhysRevApplied.9.034012

Silva, C., Azoia, N. G., Martins, M., Matama, T., Wu, J., and Cavaco-Paulo, A. (2012). “Molecular recognition of esterase plays a major role on the removal of fatty soils during detergency,” *J. Biotechnol.* 161(3), 228-234. DOI: 10.1016/j.jbiotec.2012.06.019

Simoncić, B., and Roman, V. (2007). "Wettability of cotton fabric by aqueous solutions of surfactants with different structures," *Colloids Surf. A – Physicochem. Eng. Aspects* 292(2-3), 236-245. DOI: 10.1016/j.colsurfa.2006.06.025

Sinsheimer, P., Gottlieb, R., and Farrar, C. (2002). "Integrating pollution prevention technology into public policy: The case of professional wet cleaning," *Environ. Sci. Technol.* 36(8), 1649-1655. DOI: 10.1021/es010584k

Sipponen, M. H., Lange, H., Crestini, C., Henn, A., and Osterberg, M. (2019). "Lignin for nano- and microscaled carrier systems: Applications, trends, and challenges," *ChemSusChem* 12(10), 2039-2054. DOI: 10.1002/cssc.201900480

Schmutz, A., Jenny, T., and Ryser, U. (1994). "A caffeoyl fatty-acid glycerol ester from wax associated with green cotton fiber suberin," *Phytochem.* 36(6), 1343-1346. DOI: 10.1016/S0031-9422(00)89721-6

Soljacić, I., and Pusić, T. (2004). "Wet cleaning of textiles," *Tekstil* 53(8), 392-398.

Soljacić, I., and Pusić, T. (2010). "Detergents for dry cleaning process," *Tekstil* 59(8), 348-356.

Sonesson, A. W., Callisen, T. H., Elofsson, U. M., and Brismar, H. (2007). "Imaging the detergency of single cotton fibers with confocal microscopy: The effect of surfactants and lipases," *J. Surfactants Detergents* 10(4), 211-218. DOI: 10.1007/s11743-007-1033-7

Song, J. L., Salas, C., and Rojas, O. J. (2015). "Role of textile substrate hydrophobicity on the adsorption of hydrosoluble nonionic block copolymers," *J. Colloid Interface Sci.* 454, 89-96. DOI: 10.1016/j.jcis.2015.04.061

Spitz, L. (1996). *Soaps and Detergents: A Theoretical and Practical Review*, AOCS Press, Champaign, IL.

Srivastava, V. K., Kini, G., and Rout, D. (2006). "Detergency in spontaneously formed emulsions," *J. Colloid Interface Sci.* 304(1), 214-221. DOI: 10.1016/j.jcis.2006.08.035

Stana-Kleinschek, K., Strnad, S., and Ribitsch, V. (1999). "Surface characterization and adsorption abilities of cellulose fibers," *Polymer Eng. Sci.* 39(8), 1412-1424. DOI: 10.1002/pen.11532

Strey, R. (1996). "Phase behavior and interfacial curvature in water-oil-surfactant systems," *Current Opin. Colloid Interface Sci.* 1(3), 402-410. DOI: 10.1016/S1359-0294(96)80140-3

Sutanto, S., Dutschk, V., Mankiewicz, J., van Roosmalen, M., Warmoeskerken, M. M. C. G., and Witkamp, G. J. (2014). "CO_2 dry cleaning: Acoustic cavitation and other mechanisms to induce mechanical action," *J. Supercrit. Fluids* 89, 1-7. DOI: 10.1016/j.supflu.2014.01.018

Sutanto, S., van Roosmalen, M. J. E., and Witkamp, G. J. (2013). "Redeposition in CO_2 textile dry cleaning," *J. Supercrit. Fluids* 81, 183-192. DOI: 10.1016/j.supflu.2013.05.013

Syverud, K., Xhanari, K., Chinga-Carrasco, G., Yu, Y., and Stenius, P. (2011). "Films made of cellulose nanofibrils: Surface modification by adsorption of a cationic surfactant and characterization by computer-assisted electron microscopy," *J. Nanoparticle Res.* 13(2), 773-782. DOI: 10.1007/s11051-010-0077-1

Takahashi, T., Aso, Y., and Yamamoto, T. (2007). "Detergency of electrolysis water in laundering," *Sen-I Gakkaishi* 63(5), 109-116. DOI: 10.2115/fiber.63.109

Tanaka, A., and Hoshino, E. (1999). “Study on the substrate specificity of alpha-amylases that contribute to soil removal in detergents,” *J. Surfact. Deterg.* 2(2), 193-199. DOI: 10.1007/s11743-999-0073-8

Tanford, C. (1980). *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd Ed., Wiley, New York, pp. 233.

Tanney, R. B. (2017). “Zeolite-A as a remediation technique for soil contaminated with lead,” Thesis, Ph.D., University of Kent.

Tanthakit, P., Chavadej, S., Scamehorn, J. F., Sabatini, D. A., and Tongcumpou, C. (2008). “Microemulsion formation and detergency with oily soil: IV. Effect of rinse cycle design,” *J. Surfact. Deterg.* 11(2), 117-128. DOI: 10.1007/s11743-008-1062-x

Tanthakit, P., Nakrachata-Amorn, A., Scamehorn, J. F., Sabatini, D. A., Tongcumpou, C., and Chavadej, S. (2009). “Microemulsion formation and detergency with oily soil: V. Effects of water hardness and builder,” *J. Surfact. Deterg.* 12(2), 173-183. DOI; 10.1007/s11743-009-1112-z

Tanthakit, P., Ratchatawetchakul, P., Chavadej, S., Scamehorn, J. F., Sabatini, D. A., and Tongcumpou, C. (2010). “Palm oil removal from fabric using microemulsion-based formulations,” *Journal of Surfactants and Detergents* 13(4), 485-495. DOI: 10.1007/s11743-010-1219-2

Tarasov, D., Leitch, M., and Fatehi, P. (2015). “Production of lignosulfonate in NSSC-based biorefinery,” *Biotech. Prog.* 31(6), 1508-1514. DOI: 10.1002/btpr.2149

Thompson, L. (1994). “The role of oil detachment mechanisms in determining optimum detergency conditions,” *Journal of Colloid and Interface Science* 163(1), 61-73. DOI: 10.1006/jcis.1994.1080

Timmons, C. O., and Zisman, W. A. (1968). “Relation of initial spreading pressure of polar compounds on water to interfacial tension work of adhesion and solubility,” *J. Colloid Interface Sci.* 28(1), 106-117. DOI: 10.1016/0021-9797(68)90212-9

Tongcumpou, C., Acosta, E. J., Quencer, L. B., Joseph, A.F., Scamehorn, J. F., Sabatini, D. A., Chavadej, S., and Yanumet, N. (2003a). “Microemulsion formation and detergency with oily soils: I. Phase behavior and interfacial tension,” *J. Surfact. Deterg.* 6, 191-203. DOI: 10.1007/s11743-003-0262-5

Tongcumpou, C., Acosta, E. J., Quencer, L. B., Joseph, A. F., Scamehorn, J. F., Sabatini, D. A., Chavadej, S., and Yanumet, N. (2003b). “Microemulsion formation and detergency with oily soils: II. Detergency formulation and performance,” *Surfactants and Detergents* 6(3), 205-214. DOI: 10.1007/s11743-003-0263-4

Tongcumpou, C., Acosta, E. J., Quencer, L. B., Joseph, A. F., Scamehorn, J. F., Sabatini, D. A., and Yanumet, N. (2005). “Microemulsion formation and detergency with oily soils: III. Performance and mechanisms,” *Surfactants and Detergents* 8(2), 147-156. DOI: 10.1007/s11743-005-340-8

Topalović, T., Nierstrasz, V. A., Bautista, L., Jocić, D., Navarro, A., and Warmoeskerken, M. M. C. G. (2007). “XPS and contact angle study of cotton surface oxidation by catalytic bleaching,” *Colloids Surf. A – Physicochem. Eng. Aspects* 296, 76-85. DOI: 10.1016/j.colsurfa.2006.09.026

Torn, L. H., Koopal, L. K., de Keizer, A., and Lyklema, J. (2005). “Adsorption of nonionic surfactants on cellulose surfaces: Adsorbed amounts and kinetics,” *Langmuir* 21(17), 7768-7775. DOI: 10.1021/la051102b

Touchette, R. V., and Jenness, L. C. (1960). “Effect of surface active agents on drainage and physical strength properties of sulfite pulp,” *TAPPI* 43(5), 484-489.

Traore, M. K., and Buschle-Diller, G. (1999). “Influence of wetting agents and agitation on enzymatic hydrolysis of cotton,” *Textile Chemist Colorist Amer. Dyestuff Reporter* 1(4), 51-56.

Tripathi, S. K., Tyagi, R., and Nandi, B. K. (2013). “Removal of residual surfactants from laundry wastewater: A review,” *Dispersion Sci. Technol.* 34(11), 1526-1534. DOI: 10.1080/01932691.2012.752328

Tucker, I., Petkov, J., Penfold, J., and Thomas, R. K. (2010). “Adsorption of nonionic and mixed nonionic/cationic surfactants onto hydrophilic and hydrophobic cellulose thin films,” *Langmuir* 26(11), 8036-8048. DOI: 10.1021/la1000057

UhZapata, M. U., Zhang, W., Hammouti, A., Bang, D. P., Nguyen, K. D., and Marcois, L (2022). “Two-phase experimental and numerical studies on scouring at the toe of vertical seawall,” *Eur. J. Mechanics B – Fluids* 93, 13-28. DOI: 10.1016/j.euromechflu.2021.12.008

Upadek, H., Kottwitz, B., and Schreck, B. (1996). “Zeolites and novel silicates as raw materials for detergents,” *Tenside Surfac. Deterg.* 33(5), 385-392. DOI: 10.1515/tsd-1996-330507

Uraki, Y., Koda, K., Yamada, T., Oikawa, C., and Aso, T. (2012). “Novel functions of non-ionic, amphiphilic lignin derivatives,” in: *Functional Materials from Renewable Sources*, book series: *ACS Symp. Ser.* 1107, 243. DOI: 10.1021/bk-2012-1107.ch013

van der Donck, J. C. J. (1997). “Compression of wet textile,” *Tenside Surfact. Deterg.* 34(5), 322-326. DOI: 10.1515/tsd-1997-340507

van der Donck, J. C. J. (1999). “The influence of flow through textile layers on soil removal,” *Tenside Surfact. Deterg.* 36(4), 222-224.

van der Maarel, M. J. E. C., van der Veen, B., Uitdehaag, J. C. M., Leemhuis, H., and Dijkhuizen, L. (2002). “Properties and applications of starch-converting enzymes of the alpha-amylase family,” *Biotech.* 94(2), 137-155. DOI: 10.1016/S0168-1656(01)00407-2

van Roosmalen, M. J. E., van Diggelen, M., Woerlee, G. F., and Witkamp, G. J. (2003). “Dry-cleaning with high-pressure carbon dioxide – The influence of mechanical action on washing-results,” *J. Supercrit. Fluids* 27(1), 97-108. DOI: 10.1016/S0896-8446(02)00212-7

van Roosmalen, M. J. E., Woerlee, W. F., and Witkamp, G. J. (2004). “Surfactants for particulate soil removal in dry-cleaning with high-pressure carbon dioxide,” *J. Supercrit. Fluids* 30(1), 97-109. DOI: 10.1016/S0896-8446(03)00115-3

Vaughn, T. H., and Smith, C. E. (1948). “The effect of sodium carboxymethyl cellulose on synthetic detergent systems,” *J. Amer. Oil Chemists Soc.* 25(2), 44-51. DOI: 10.1007/BF02593188

Vera, R. E., Salazar-Rodríguez, F., Marquez, R., and Forgiarini, A. M. (2020a). “How the influence of different salts on interfacial properties of surfactant–oil–water systems at optimum formulation matches the Hofmeister series ranking,” *Journal of Surfactants and Detergents* 23(3), 603-615. DOI: 10.1002/jsde.12406

Vera, R. E., Suarez, A., Zambrano, F., Marquez, R., Bedard, J., Vivas, K., Pifano, A., Farrell, M., Ankeny, M., Jameel, H., and Gonzalez, R. (2022a). “Upcycling cotton textile waste into bio-based building blocks through an environmentally friendly and high-yield conversion process,” Available at SSRN: https://ssrn.com/abstract=4156353 or DOI: 10.2139/ssrn.4156353

Vera, R. E., Zambrano, F., Suarez, A., Pifano, A., Marquez, R., Farrell, M., Ankeny, M., Jameel, H., and Gonzalez, R. (2022b). “Transforming textile wastes into biobased building blocks via enzymatic hydrolysis: A review of key challenges and opportunities," submitted to: *Cleaner and Circular Bioeconomy*.

Visser, J. (1995). "Particle adhesion and removal: A review," *Particulate Sci. Technol.* 13(3-4), 169-196. DOI: 10.1080/02726359508906677

Vivod, V., Neral, B., Mihelic, A., and Kokol, V. (2019). "Highly efficient film-like nanocellulose-based adsorbents for the removal of loose reactive dye during textile laundering," *Textile Res. J.* 89(6), 975-988. DOI: 10.1177/0040517518760752

Vollhardt, D., and Fainerman, V. B. (2006). "Progress in characterization of Langmuir monolayers by consideration of compressibility," *Adv. Colloid Interface Sci.* 127(2), 83-97. DOI: 10.1016/j.cis.2006.11.006

Wang, Z. J., Lan, T. Q., and Zhu, J. Y. (2013). "Lignosulfonate and elevated pH can enhance enzymatic saccharification of lignocelluloses," *Biotech. Biofuels* 6, article no. 9. DOI: 10.1186/1754-6834-6-9

Wang, J. J., Zhang, J. F., Feng, P. F., and Guo, P. (2018). "Damage formation and suppression in rotary ultrasonic machining of hard and brittle materials: A critical review," *Ceramics Int.* 44(2), 1227-1239. DOI: 10.1016/j.ceramint.2017.10.050

Warmoeskerken, M. M. C. G., van der Vlist, P., Moholkar, V. S., and Nierstrasz, V. A. (2002). "Laundry process intensification by ultrasound," *Colloids Surf. A – Physicochem. Eng. Aspects* 210(2-3), 277-285. DOI:10.1016/S0927-7757(02)00372-2

Warne, M. S. J., and Schifko, A. D. (1999). "Toxicity of laundry detergent components to a freshwater cladoceran and their contribution to detergent toxicity," *Ecotox. Environ. Safety* 44(2), 196-206. DOI: 10.1006/eesa.1999.1824

Willke, Th., and Vorlop, K.-D. (2001). "Biotechnological production of itaconic acid," *Applied Microbiology and Biotechnology* 56(3), 289-295. DOI: 10.1007/s002530100685

Wilmarth, W. W. (1975). "Structure of turbulence in boundary layers," *Adv. Appl. Mech.* 15, 159-254. DOI: 10.1016/S0065-2156(08)70057-7

Wingrave, J. A. (1984). "Linear sodium alkylbenzene sulfonate homologs - Comparison of detergency performance with experimental and thermodynamic wetting theories," *ACS Symp. Ser.* 253, 241-268. DOI: 10.1021/bk-1984-0253.ch016

Witthayapanyanon, A., Harwell, J. H., and Sabatini, D. A. (2008). "Hydrophilic–lipophilic deviation (HLD) method for characterizing conventional and extended surfactants," *Journal of Colloid and Interface Science* 325(1), 259-266. DOI: 10.1016/j.jcis.2008.05.061

Woods, D. A., Petkov, J., and Bain, C. D. (2011). "Surfactant adsorption by total internal reflection Raman spectroscopy. Part III: Adsorption onto cellulose," *Colloids Surf. A – Physicochem. Eng. Aspects* 391, 10-18. DOI: 10.1016/j.colsurfa.2011.07.027

Xu, C., and Ferdosian, F. (2017). *Conversion of Lignin into Bio-Based Chemicals and Materials*, series: *Green Chemistry and Sustainable Technology*, Springer. DOI: 10.1007/978-3-662-54959-9

Yamane, C., Aoyagi, T., Ago, M., Sato, K., Okajima, K., and Takahashi, T. (2006). "Two different surface properties of regenerated cellulose due to structural anisotropy," *Polym. J.* 38(8), 819-826. DOI: 10.1295/polymj.PJ2005187

Yun, C., Park, S., and Park, C. H. (2013). "The effect of fabric movement on washing performance in a front-loading washer," *Textile Res. J.* 83(17), 1786-1795. DOI: 10.1177/0040517512452927

Yun, C., Cho, Y., and Park, C. H. (2017). "Washing efficiency and fabric damage by beating and rubbing movements in comparison with a front-loading washer," *Textile Res. J.* 87(6), 708-714. DOI: 10.1177/0040517516636005

Yun, C., and Park, C. H. (2015a). "The effect of fabric movement on washing performance in a front-loading washer. II: Under various physical washing conditions," *Textile Res. J.* 85(3), 251-261. DOI: 10.1177/0040517514545260

Yun, C., and Park, C. H. (2015b). "The effect of fabric movement on washing performance in a front-loading washer. III: Focus on the optimized movement algorithm," *Textile Res. J.* 86(6), 563-572. DOI: 10.1177/0040517515590417

Zambrano, M. C., Pawlak, J. J., Daystar, J., Ankeny, M., Cheng, J. J., and Venditti, R. A. (2019). "Microfibers generated from the laundering of cotton, rayon and polyester based fabrics and their aquatic biodegradation," *Marine Pollution Bulletin* 142, 394-407. DOI: 10.1016/j.marpolbul.2019.02.062

Zana, R. (1996). "Critical micellization concentration of surfactants in aqueous solution and free energy of micellization," *Langmuir* 12(5), 1208-1211. DOI: 10.1021/la950691q

Zarate-Muñoz, S., de Vasconcelos, F. T., Myint-Myat, K., Minchom, J., and Acosta, E. J. (2016). "A simplified methodology to measure the characteristic curvature (CC) of alkyl ethoxylate nonionic surfactants," *Journal of Surfactants and Detergents* 19(2), 249-263. DOI: 10.1007/s11743-016-1787-x

Zeng, Y. N., Zhao, S., Yang, S. H., and Ding, S. Y. (2014). "Lignin plays a negative role in the biochemical process for producing lignocellulosic biofuels," *Current Opin. Biotech.* 27, 38-45. DOI: 10.1016/j.copbio.2013.09.008

Zhang, Y. N., Zhang, M. M., Reese, R. A., Zhang, H. Q., and Xu, B. Q. (2016). "Real-time single molecular study of a pretreated cellulose hydrolysis mode and individual enzyme movement," *Biotech. Biofuels* 9, article no. 85. DOI: 10.1186/s13068-016-0498-x

Zhou, H. F., Lou, H. M., Yang, D. J., Zhu, J. Y., and Qiu, X. Q. (2013). "Lignosulfonate to enhance enzymatic saccharification of lignocelluloses: Role of molecular weight and substrate lignin," *Indust. Eng. Chem. Res.* 52(25), 8464-8470. DOI: 10.1021/ie401085k

APPENDIX

Table A. Some Definitions Pertaining to Detergency

Term	Definition
Bleach	A chemical that is capable of changing a colored organic compound (a chromophore) into a non-colored compound
Buffer	A substance present in water that tends to minimize changes in pH upon addition of small amounts of either a strong acid or a strong base to the mixture
Builder	A substance such as Zeolite A, sodium tripolyphosphate (STPP), or carboxymethylcellulose (CMC) that is capable of improving the performance of a detergent system, especially in the presence of hard water
Cellulosic	Having its origins in a plant material such as wood, cotton, bacterial cellulose, *etc.*, often with some residual contents of hemicellulose and lignin
Chelating agent	A chemical compound having very high complexing ability with multivalent metal ions, usually due to the presence of four or more carboxylate groups that are capable of surrounding the ion of interest
Cloud point	The temperature above which the surfactant becomes insoluble, thus giving rise to increased turbidity of the mixture
Colloidal	Having to do with suspensions of particles or droplets smaller than about 5 µm, such that their behavior is dominated by short-range forces, mainly electrostatic (double-layer) and van der Waals (London dispersion)
Critical micelle concentration (CMC)	The concentration in aqueous solution above which micelles will be present and in equilibrium with the surfactant molecules present as individuals in solution
Curvature	The tendency of a given surfactant, under defined conditions of salinity, to form a curved surface, as might be suited for forming either a water-in-oil or oil-in-water emulsion
Detergent	A formulation of a surface-active compound, together with other ingredients, to promote the release of dirt and other contaminants from solid surfaces such as cloth
Dirt	For purposes of the present article, any substance – solid-like or liquid-like – that is undesirably present on or within material that is to be washed using a detergent solution
Dry cleaning	Use of a non-aqueous medium such as perchloroethylene, usually with addition of a suitable surfactant, for laundering
Emulsification of oily dirt	A mechanism by which an oily dirt particle becomes engulfed by a micelle or hemimicelle, followed by roll-up detachment
Emulsion	A very small droplet of oily material that is stabilized in aqueous solution by a monolayer of surfactant molecules
Entrapped state	Location of a dirt particle or droplet between fibrils or within strands, *etc.*, such that deformation or dissolution of the dirt would be the only path to effective removal
Enzyme	A large protein structure, usually obtained from bacteria or fungi, having the ability to catalyze one or more chemical reactions
Extended surfactants	Anionic surfactants that have a few ethylene oxide units interposed between a hydrophilic group (*e.g.* sulfate or ethylene oxide chain) and a hydrophobic alkyl group
Finishing (or sizing)	Application of a solution onto filaments or yarns of textile fiber, followed by drying, as a means to facilitate processing or to develop desired attributes in the resulting textile product
Hardness of water	The concentration of calcium plus magnesium divalent ions in water

Hydrodynamic shear	A change in velocity within a fluid as a function of distance at a right angle to the direction of flow
Hydrophilic-lipophilic balance (HLB)	For a typical nonionic surfactant comprising an ethylene oxide chain (hydrophilic) and an alkyl chain (hydrophobic), 20 times the ratio between the molecular mass of the hydrophilic part and the total molecular mass
Hydrophilic-lipophilic difference (HLD)	A semiempirical equation involving salinity, type of head group, type of oil, type of alcohol, and temperature difference relative to 25 °C
Hydrophobic effect	A tendency of hydrophobic groups to self-associate, often at interfaces or within micelles, such as to minimize their getting in the way of hydrogen bonding opportunities involving water molecules
Interfacial rigidity	A tendency within a surfactant monolayer film to resist stretching or deformation, as in the extreme case of aluminum stearate monolayer films
Ion exchange	The tendency of ionically charged materials to interact more strongly with oppositely charged ions that have higher valency
Laundering	A process whereby articles of clothing and other textile items are immersed in a detergent solution, followed by rinsing and drying
Linker, lipophilic	A relatively short compound that usually comprises an ethylene oxide chain and an alkyl chain
Mercerization	Treatment of a cellulose-based material with sufficiently strong sodium hydroxide (*e.g.* 24%) to render it more suitable for certain textile items, in which the crystal form has been mainly changed to cellulose II
Micelle	An arrangement of surfactant molecules in aqueous media such that hydrophobic tails self-associate and the hydrophilic headgroups generally face outwards
Peptization	A term from the field of colloidal chemistry indicating that the aqueous conditions have been changed, *e.g.* by increasing the pH or adding a dispersant, such that the adhering dirt particles are electrostatically repelled from the substrate and become released
Phase inversion temperature (PIT)	The temperature above which various emulsion phases can become prominent in aqueous surfactant mixtures
Plasticization	The effect of adding a compound (such as water, ethylene glycol, *etc.*) to a dirt particle such that it becomes more deformable when acted upon continuously by a force
Progressive adsorption and stabilization	A mechanism by which wiggling of an attached dirt particle may facilitate progressive migration of surfactant molecules to locations between the dirt and the substrate, thereby facilitating detachment and suspension
Redeposition	The attachment of dirt particles or oily droplets back onto a substrate after having been initially detached, usually by action of a detergent system. For example, redeposition can be associated with dilution during a rinsing cycle.
Regenerated cellulose	The product obtained by first dissolving cellulose (*e.g.* by the viscose process or the lyocell process) and then changing the medium such that the material comes back out of solution as cellulose (cellulose II crystal form)
Rolling release	A mechanism of particle detachment in flow for which the rate-determining step involves an incipient rolling motion
Roll-up	A mechanism of detergent action whereby the very low interfacial tension associated with microemulsion formation allows a condensed monolayer of surfactant at an interface between a substrate and contaminate to roll up from the substrate, such that the dirt is released
Sizing (or finishing)	Application of a solution onto filaments or yarns of textile fiber, followed by drying, as a means to facilitate subsequent processing or to develop desired attributes in the resulting textile product

Snap-off	A mechanism of detergent action whereby the very low interfacial tension associated with microemulsion formation allows a condensed monolayer of surfactant adsorbed onto an oily contaminant to neck and then be pinched off, resulting in detachment of an emulsion droplet, which contains some of the oily contaminant
Soap	The sodium salt of a fatty acid or other molecule that forms micelles in solution and exhibits a washing ability in aqueous systems having low water hardness
Softening of fabric	The effects of certain cationic surfactant molecules that are selected for their ability to resist the formation of hydrogen bonds between adjacent cellulosic surfaces during the evaporative drying or a textile item
Softening of water	Reduction in the effective concentration of Ca^{2+} and Mg^{2+} ions in solution, often as a result of their adsorption onto a substrate bearing carboxylate groups initially associated with sodium ions
Solubilization	A mechanism by which dirt is chemically changed and converted to a soluble or very finely dispersible form, as in the case of saponification or enzymatic hydrolysis
Stains	Persistent discolorants that are often difficult to remove from fabric by ordinary laundering
Sublayer of turbulent flow	A dominance of local rectilinear flow very near to a flat surface that is exposed to turbulent shear flow
Supercritical CO_2	Carbon dioxide having a suitably high pressure (74+ atmospheres) and temperature (30+ °C) so that it has properties in between those of a gas and a liquid
Surfactant	A molecule having one part that is attracted to an aqueous phase and another part attracted to an oily phase such that it has a tendency to be present at interfaces, including the water-air interface and the water-dirt interface
Wet cleaning	Use of a water-containing liquid formulation in an industrial process (not for home usage) aimed at achieving levels of cleaning comparable with those expected from dry cleaning
Wetting	The tendency of a liquid to spread into molecular contact over the surface of a solid material. In the case of a wettable surface (defined in reference to a probe liquid), the angle of contact (drawn through the liquid phase) is less than 90 degrees.
Winsor conditions	The phase behavior that can be observed after shaking water, an oil, and a surfactant in a capped vial, then observing its separation into one, two, or three phases
Zeolite	An aluminum silicate crystalline mineral having highly regular micropores, often in a suitable size to bind hardness ions