

# 5

## Rheology Modifiers and Thickeners for Liquid Detergents

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### I. INTRODUCTION

Liquid detergents make a major contribution to the overall detergent and cleaners market, due in part to their handling characteristics and their ease of use. However, in numerous cases, the formulations would lack either consumer appeal or essential physical properties if they did not include additives to modify their viscosity or rheology. Generally speaking, viscosity build is required to improve the aesthetics of a formulation and meet the demands of consumers, for whom the concept “thicker is better” often remains valid [1]. This is especially true in those liquid formulations where the resulting viscosity without additives is barely above that of water itself. A simple increase in viscosity, though, is often not sufficient to meet the technical demands of a formulation. To address these needs, the rheology of the system has to be taken into consideration, and this is intimately bound up with the nature of the formulation, as well as its intended delivery system and its use.

Thus, a scouring cream will require suspending properties to prevent the finely divided abrasive from precipitating, yet it must be pourable or squeeze-dispensable from its package. Similarly, a spray cleaner will require a low viscosity under conditions of high shear in order to facilitate the passage through the spray or trigger mechanism. In the case of a wall or bathroom cleaner, a certain degree of “vertical cling” will be needed to maximize the contact time between the formulation and the surface. All these properties can be obtained through the appropriate choice of rheology modifiers [2].

The selection of the most suitable rheology modifier will depend on the type of flow, or rheology, required, based on considerations such as those indicated above. This will be largely, but not exclusively, an inherent property of the modifier itself. Selection will also depend to some extent on the nature of the formulation, as not all rheology modifiers are necessarily physically or chemically compatible with all other formulation components. For example, anionically charged rheology modifiers are often precluded from use in cationic-based systems such as fabric softeners in order to avoid incompatibilities with the surfactant. Even presuming compatibility, the other components of a formulation can alter the rheological properties of the additive being used, particularly if this is an associative rheology modifier. Clarity can be another issue with certain additives *per se*, or in combination with different ingredients. Bentonite, which is useful for contributing to the suspending properties of a formulation, gives opacity. Polyacrylic acids, whereas clear in aqueous solution, may show lack of clarity when certain surfactants are present.

In the case of liquid detergents, surfactants are almost always present. At low to intermediate concentration, most neat surfactant solutions have low viscosity and are close to Newtonian in flow. Only at higher surfactant concentrations, when structured micellar bilayers and other complex phases are formed, do systems tend to differ greatly from Newtonian. This behavior also helps drive the viscosity of finished formulations. In the great majority of liquid detergent formulations, concentrations of surfactant are such that little structure is developed by the surfactants themselves, resulting in formulations of low viscosity. As such, thickeners and/or rheology modifiers are often required to obtain the desired viscosity and flow characteristics.

In this chapter we survey the most common types of rheology modifiers that are used today in liquid detergents. This covers both natural and synthetic modifiers, with numerous subclasses in each, as illustrated in [Table 5.1](#). Guidelines for the types of rheological profiles each modifier can provide, as well as general formulation issues, are presented.

## II. RHEOLOGY

When a stress is applied to a liquid it will begin to deform, or flow. The deformation per unit of time, referred to as the shear rate, will increase as the applied stress

**TABLE 5.1** Classification of Various Types of Organic and Inorganic Rheology Modifiers**Organic thickeners**

## Nonassociative

## Naturally derived

Nonionics (e.g., hydroxyethyl cellulose), anionic (e.g., carboxymethyl cellulose)

Other polysaccharides (e.g., xanthan)

Miscellaneous (e.g., alginates)

## Synthetic

Nonionics (e.g., polyvinyl alcohol)

Alkali swellables (e.g., crosslinked acrylics)

Alkali solubles (e.g., noncrosslinked acrylics)

## Associative

## Naturally derived

Nonionics (e.g., hydrophobically modified hydroxyethyl cellulose, HMHEC)

## Synthetic

Nonionics (e.g., hydrophobically modified ethoxylated urethanes, HEUR;  
hydrophobically modified nonionic polyols, HNP)

Anionics (e.g., hydrophobically modified alkali-soluble emulsions, HASE)

**Inorganic thickeners**

Salts (e.g., sodium chloride, magnesium chloride)

Clays (e.g., bentonite, hectorite)

increases. If the relationship between increasing applied stress and increasing shear rate is linear, then the liquid is defined as Newtonian, and the viscosity is the slope of the plot of shear rate against applied stress. As the relationship is linear, then the slope is constant, and so the viscosity is independent of the shear rate (Figure 5.1).

In reality, few systems are Newtonian, and some of the other principal rheological profiles are also shown in Figure 5.1. In many cases a Newtonian behavior is not desirable for a formulated product. This can be illustrated by the case of a spray cleaner. A certain minimum viscosity is often required such that the material appears to be “concentrated” in the bottle. The visual appearance is referred to in this chapter as the “apparent viscosity” and is generally considered to correspond to a shear rate of the order of  $10 \text{ sec}^{-1}$  (reciprocal seconds). If the formulation is Newtonian, then the viscosity will remain the same even at the relatively high shear rates corresponding to spraying (Figure 5.2). This is not desirable, as the spray pattern obtained varies considerably with the viscosity of the fluid in the spray nozzle, and better atomization is observed when the viscosity is low. Consequently, an ideal profile for such a formulation is one in which the viscosity decreases as

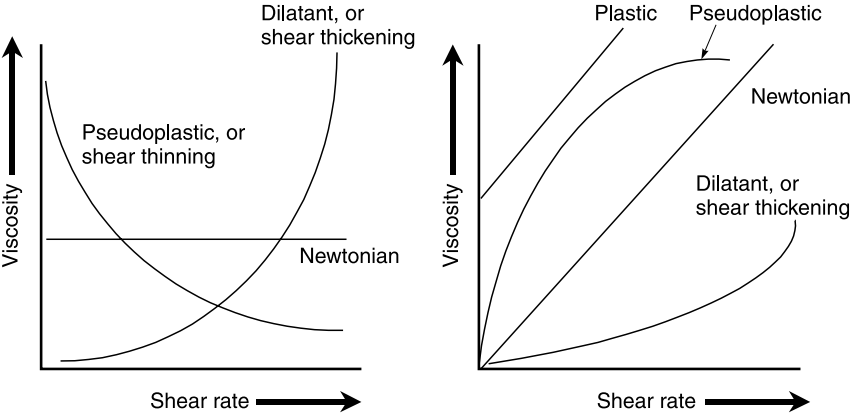


FIG. 5.1 Illustrative examples of various rheological responses.

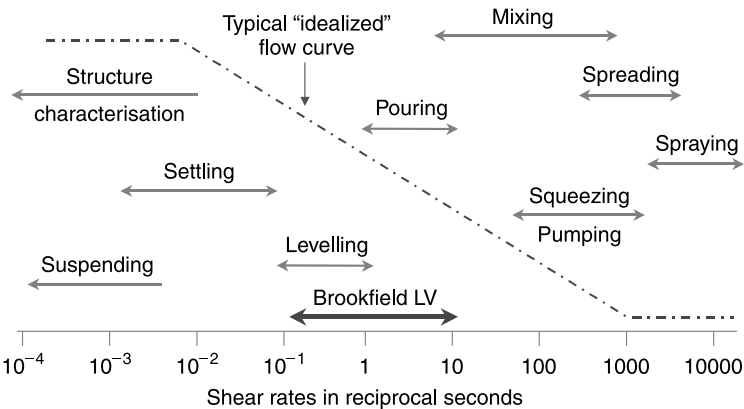
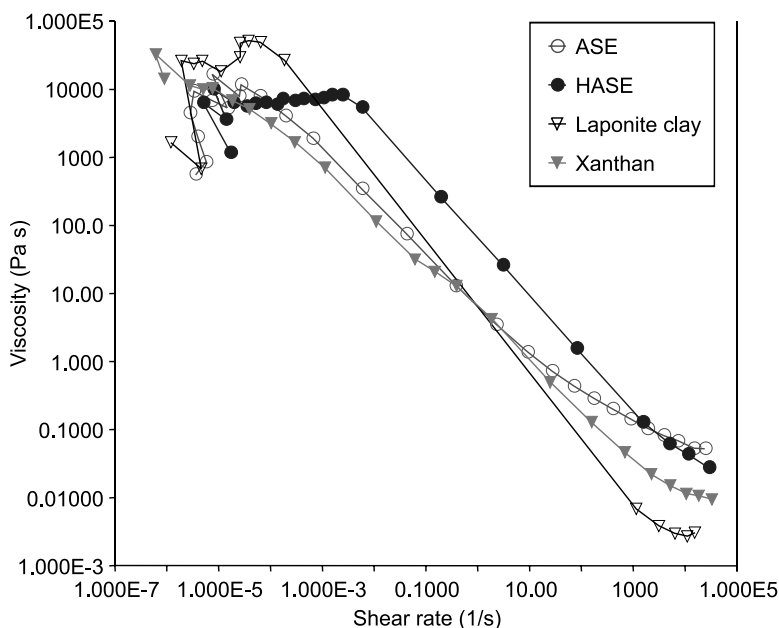


FIG. 5.2 Various flow events and their link to typical shear rate ranges.

the shear rate increases, as shown in Figure 5.1. Such a fluid is described as shear thinning, or pseudoplastic, and the degree of pseudoplasticity can be adjusted by the choice of rheology modifier. Figure 5.3 shows the viscosity response for aqueous solutions of four different rheology modifiers. Note the differences in the shear rate dependences of the solutions, with the Laponite being the most pseudoplastic of the four.

In the case of suspensions, be they opaque dispersions of abrasives found in certain scouring creams, or the suspension of visual cues or active ingredients now



**FIG. 5.3** Measured flow curves for aqueous solutions of four common types of rheology modifiers. ASE is an alkali swellable/soluble emulsion-type rheology modifier and HASE is a hydrophobically modified alkali-soluble emulsion.

encountered in transparent hand, dish, and toilet cleaners, the properties required from the rheology modifier must ensure no settling of the components in the bottle. There are several techniques used to evaluate whether or not a formulation will adequately suspend ingredients, and it is not intended to evaluate the merits of each here. One of the simplest methods to use is the Brookfield yield value, which is a useful comparative tool, and in many cases is certainly sufficient to obtain a good approximation of the suspending properties of a system. This is evaluated by measuring the Brookfield viscosity at 0.5 and 1 rpm, and then calculating the yield value (YV) as:

$$\text{YV} = \frac{\text{viscosity (0.5 rpm)} - \text{viscosity (1 rpm)}}{100}$$

More sophisticated techniques use a controlled stress rheometer to evaluate the minimum stress necessary to obtain flow (the yield stress) or to calculate, by appropriate modeling, the zero shear viscosity of the system. Whichever technique

is employed, the yield stress/value required to achieve a stable suspension will be greater as the size of the particle to be suspended increases, and as the density difference between the matrix and the particle increases.

### III. ORGANIC THICKENERS

Within the group of polymers classified under the heading of organic thickeners, there are both associative and nonassociative variants of several of the polymers. Associative rheology modifiers are those polymers that contain hydrophobic moieties at various levels in their composition. If this modification is made to a high-molecular-weight polymer, then it gives rise to an additional mechanism for modifying the rheological characteristics of the matrix. As well as the swelling and/or chain entanglement that occurs with polymers of a high molecular weight, inter- or intramolecular hydrophobic association can also take place in aqueous media. This is similar to the hydrophobic association that takes place in aqueous surfactant solutions, and which drives the surfactant molecules to form micelles. In the case of associative polymers, these interactions can take place between the polymer molecules, with other hydrophobes present in the matrix, including surfactants, or even with certain particle surfaces. By associating with other components in the system, additional structure can be developed which can modify rheology, and also contribute to the overall stability of the matrix.

#### A. Acrylics

A wide range of acrylic-derived polymers is available, and they can be classified in various ways. There are homopolymers and copolymers, and they can be emulsion polymerized (in water) or inverse polymerized (in an organic solvent). In addition they can be associative or nonassociative. Different acronyms and nomenclatures are used to describe the various classes of polymers. Some of the earliest acrylic rheology modifiers were the carbomers, which are crosslinked homopolymers of polyacrylic acid manufactured by inverse polymerization in a suitable solvent. They are generally recovered from the solvent by precipitation and are available as powders. A second class of nonassociative acrylic rheology modifiers are the alkali swellable/soluble emulsion (ASE) polymers which is subdivided into two categories. There are both crosslinked and noncrosslinked ASE polymers, which are essentially acrylic copolymers produced by aqueous (emulsion) polymerization and which are in the form of low-viscosity aqueous dispersions. The different product forms of the various classes of polymer can have an impact on the choice of the most suitable additive for a given situation. The equipment required for handling the aqueous-based emulsion polymers is simpler than that required for handling powders, in particular since polyacrylic acid-based powders

are hygroscopic. The water-based emulsion polymers also show an advantage for high-throughput systems, as they can be integrated into continuous manufacturing processes, which is more difficult with a powdered additive.

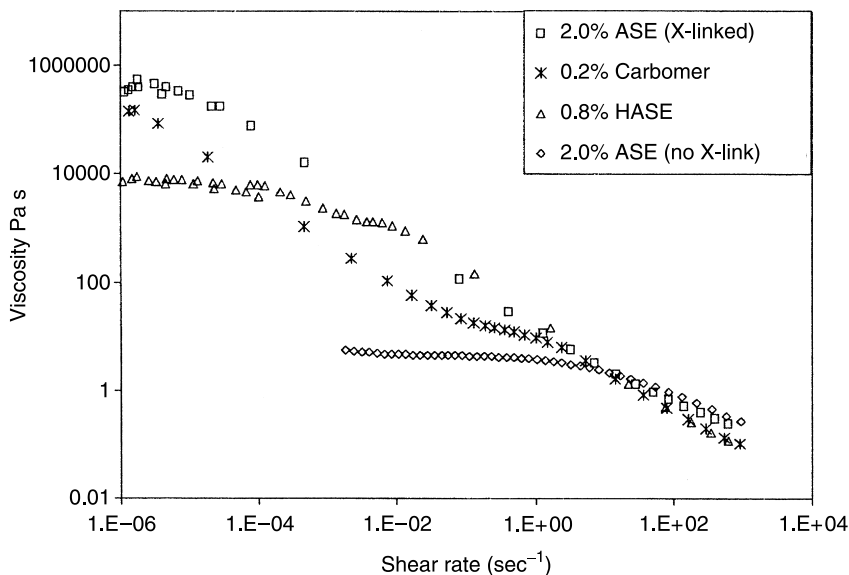
Both of the types of polymer mentioned above can be modified by the incorporation of hydrophobic monomers onto the essentially hydrophilic acrylate backbone. The effect of this is to modify their characteristics by giving them so-called “associative” properties. These hydrophobes can interact or “associate” with other hydrophobes in the formulation (e.g., surfactants, oils, or hydrophobic particles) and thus build additional structures in the matrix [3–11]. These associative polymers are termed cross-polymers when they are based on carbomer-type chemistry [12] and hydrophobically modified alkali-soluble emulsions (HASEs) when based on ASE technology.

Although all of these additives are based on acrylic chemistry, both the behavior and the performance of the different categories of polymer vary considerably. One point in common, however, is that they are nearly all supplied in the acidic form and require neutralization to develop their thickening and rheological properties. The precise pH range over which these properties are obtained varies with the composition of the material, but in general the carbomers and the cross-polymers begin to develop their rheology-modifying behavior at a pH value of about 1 to 2 units below that of the ASE and HASE polymers.

The simplest system to consider is represented by a dispersion of the neutralized polymer in water. All show excellent clarity, but the carbomers (and the cross-polymers, not shown) are undoubtedly the most efficient in terms of their simple aqueous thickening properties, as indicated in Figure 5.4. The quantity of polymer required to achieve a given mid-shear rate viscosity is close to an order of magnitude less than that required for a crosslinked ASE thickener. The HASE polymers are generally found to have an efficiency between that of the ASE and the carbomer/cross-polymers.

The shape of the aqueous rheology curve also varies with the nature of the polymer. Both the carbomers and the cross-polymers show fairly similar behavior. Crosslinked ASE polymers, as shown in Figure 5.4, show a profile close to that of the carbomers, giving highly shear-thinning properties, although this is to some extent dependent on molecular weight. A noncrosslinked ASE polymer shows a more Newtonian profile. The HASE polymers tend to show a behavior between that of a noncrosslinked ASE thickener and the carbomers or crosslinked ASE polymers.

Build of significant low shear viscosity is used in many applications, and contributes significantly to formulation properties such as the vertical cling and the ability to suspend particles in a matrix. The obvious use of particle suspension is in slurries, where stability of the suspension over time is required. However, it is clear that this ability to suspend can also be applied to emulsions, which are simply suspensions of one immiscible liquid phase in another. As such, acrylic polymers



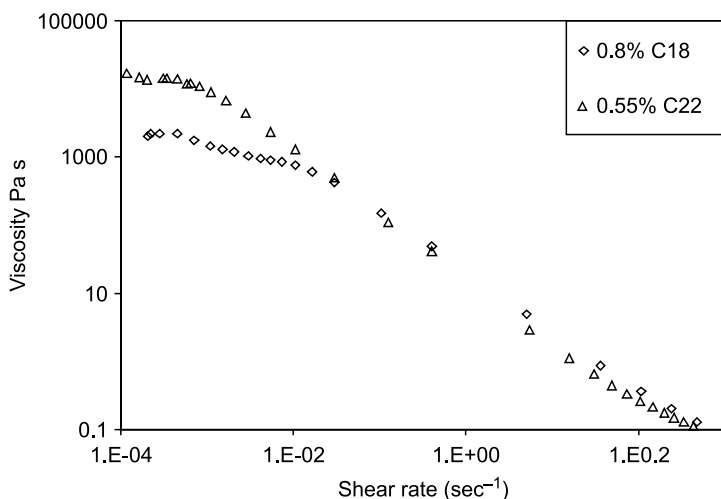
**FIG. 5.4** Measured flow curves for aqueous solutions of four different acrylic thickeners.

showing low shear viscosity build can be very useful additives for stabilizing liquid–liquid emulsions and solid–liquid dispersions.

In HASE polymers the nature of the hydrophobe has a significant impact on both the efficiency and the pseudoplasticity of the resulting aqueous solution [13]. The longer the hydrophobe chain, and, within limits, the greater the number of hydrophobes on the polymer backbone, the greater the efficiency and the more pseudoplastic the polymer. This is illustrated in [Figure 5.5](#), where the medium and high shear viscosities of the two polymers are equivalent. The two HASE polymers vary by the length of the hydrophobic moieties, C18 vs. C22. To obtain these results, a significantly lower content of the more hydrophobic HASE is required (0.55% vs. 0.8% for the less hydrophobic variant). In addition, the more hydrophobic C22 HASE polymer remains pseudoplastic over a wider shear rate range.

The above guidelines for the acrylic rheology modifiers are most useful in simple systems that are mainly water. However, in more complex matrices such as many finished formulations the situation can be very different. Both the carbomer and the cross-polymer type of rheology modifier are very sensitive to the presence of electrolytes, and this has a dramatic effect on the efficiency of the polymer, as well as on clarity. It is frequently found that in systems containing electrolytes, be they inorganic salts or anionic surfactants, the efficiency of a crosslinked ASE





**FIG. 5.5** Measured flow curves for aqueous solutions of two different HASE polymers, illustrating the effect of hydrophobe size (see legend) on the low shear rate viscosity.

(x-ASE) or a HASE can often be as good if not better than a carbomer or a cross-polymer. This can also frequently be allied with a better formulation clarity.

Whereas in simple aqueous solutions the carbomers and the cross-polymers show a significantly better efficiency, Table 5.2 shows that in surfactant-based systems this no longer holds true. The use levels indicated in the table are the quantities of polymer required to obtain a given apparent Brookfield LV-60 viscosity of about 3000 mPa s, and in all the anionic surfactants the results are more equitable for the different classes of polymer compared with the situation in water. In the case of the nonionic surfactant, the difference is still maintained, however.

In terms of clarity, though, there is a notable advantage when using a HASE polymer in place of other acrylic polymers. Clarity is measured as the optical density, and from Table 5.2 the better clarity of the surfactants thickened with the HASE polymer is apparent. An optical density of 0.05 or less can be considered clear, and between 0.05 and 0.075 as showing a very slight haze. Above a value of 0.1 a loss of clarity becomes easily apparent.

In terms of the overall rheology profile of acrylic polymers when used in finished formulations, the behavior of the nonassociative thickeners is relatively easy to predict, as there is little interaction from a rheological point of view between the thickener and the matrix. Significantly higher polymer levels will be required if electrolytes are present, but the overall formulation rheology (e.g., pseudoplasticity, yield development) will remain similar. In most circumstances, though,

**TABLE 5.2** Use Level (% Solids Based on Total) Required of Four Rheology Modifiers to Obtain a Surfactant Solution with Brookfield Viscosity of 3000 mPa s, and the Measured Clarity Values (Optical Density) of these Solutions

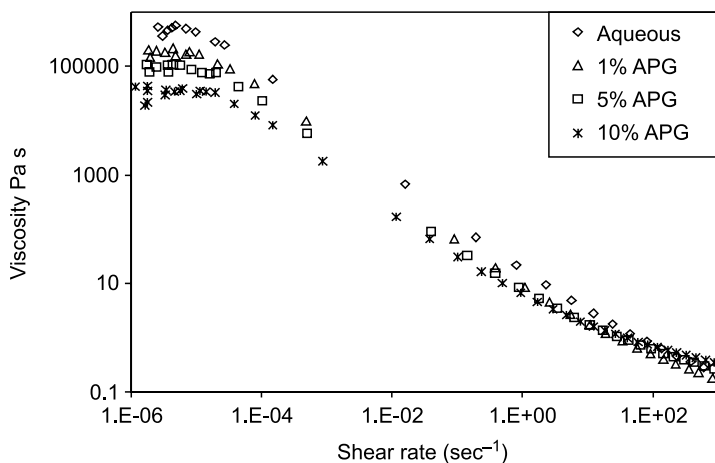
Surfactant	HASE	x-ASE	Cross-polymer	Carbomer
10% SLES				
Use level	1.1	4.5	1.2	1.6
Clarity	0.05	0.33	0.30	1.30
10% SLS				
Use level	1.35	3.0	1.1	1.4
Clarity	0.03	0.28	0.15	0.70
5% CAPB				
Use level	1.75	2.1	1.0	1.2
Clarity	0.05	2.36	0.16	0.83
5% SLES				
Use level	1.05	3.7	1.1	1.3
Clarity	0.03	0.18	0.13	0.81
5% APG				
Use level	1.7	2.0	0.4	0.5
Clarity	0.02	0.01	0.19	0.84

Surfactants: anionics sodium lauryl ether sulfate (SLES) and sodium lauryl sulfate (SLS); amphoteric cocamidopropyl betaine (CAPB); nonionic alkyl polyglucoside (APG).

HASE, hydrophobically modified alkali-soluble emulsion; x-ASE, crosslinked alkali swellable/soluble emulsion.

the clarity of the formulation will decrease as the electrolyte content increases, particularly in the case of the carbomers. Additionally, the ultimate stability of the formulation may be suspect.

The cross-polymers show rheology similar to that found in water, albeit at markedly reduced efficiency, and with some loss in clarity. However, the absence of clarity is not so great as that found with the carbomers. This improvement in clarity, but with little change in rheology, is attributed to the fact that these cross-polymers contain relatively small amounts of hydrophobe. The HASE polymers generally show good compatibility with electrolytes with little loss of clarity and efficiency. Nevertheless, the relatively high hydrophobe content of these polymers leads to strong associations between the polymer and the hydrophobes of the surfactant, and hence the rheology of the HASE polymers in surfactant solutions tends to differ significantly from the behavior found in water. This change depends to some extent on the surfactant, but also on the nature and quantity of the hydrophobe present on the polymer. It is sometimes found judicious to blend polymers of differing characteristics in order to achieve the required physical properties in a finished formulation.

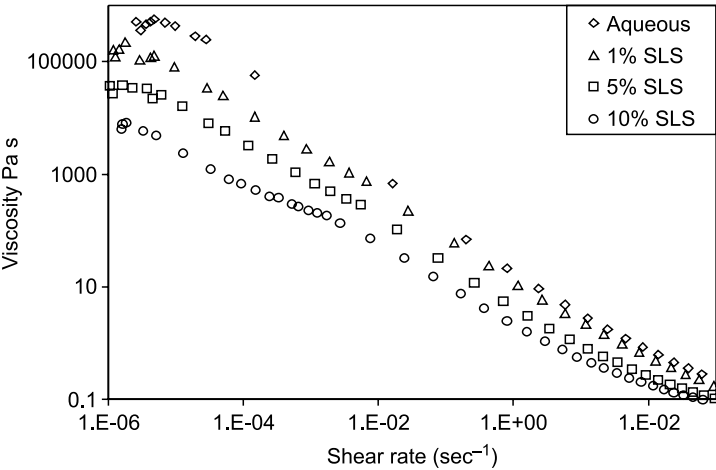


**FIG. 5.6** Measured flow curves for a crosslinked ASE polymer in solutions of increasing alkyl polyglucoside (APG) concentration.

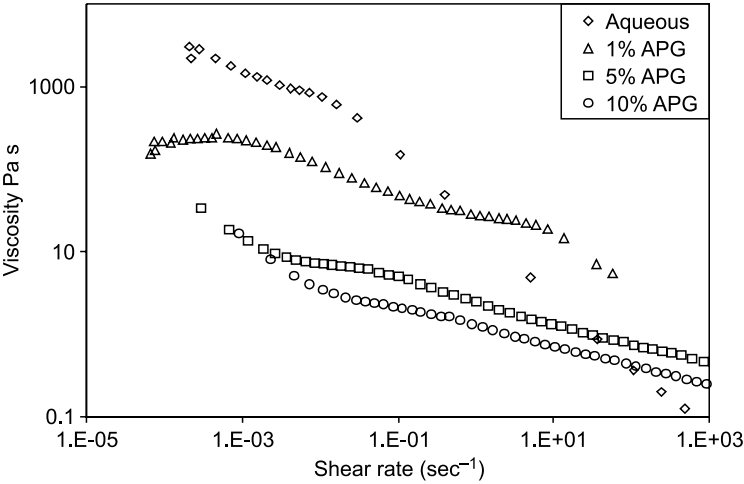
In the following examples some of the matrix effects observed between rheology modifiers and different surfactants are illustrated. The case of a crosslinked ASE polymer in the presence of a nonionic alkyl polyglucoside (APG) surfactant is shown in Figure 5.6. The rheological profiles of the polymer in different concentrations of APG are very similar to those of the aqueous polymer results, indicating that the surfactant has very little effect on the rheological behavior of the ASE polymer.

The situation is a little different in the case of a crosslinked ASE with an anionic surfactant such as sodium lauryl sulfate (SLS), as shown in Figure 5.7. The overall shapes of the curves at the different SLS contents are similar to that of the aqueous solution. However, the curves are shifted downwards, illustrating a loss in efficiency of the polymer. This, however, is not a surfactant effect, but an electrolyte effect, showing how the ionic strength of the matrix is reducing the swelling of the polymer and reducing its efficiency.

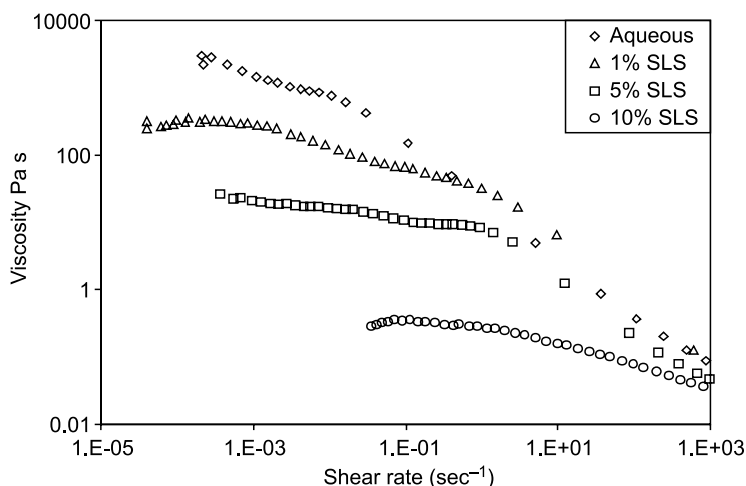
The case of a HASE polymer is different, as illustrated in Figure 5.8 and Figure 5.9. Here the overall profiles of the rheological curves are significantly altered in the presence of the different surfactants, the system becoming less pseudoplastic as the surfactant concentration increases [14,15]. It is interesting to note that in this case the efficiency of the polymer varies with the shear rate. At low shear rates the viscosity shows a decline as the surfactant content increases, but at higher shear rates the surfactant–polymer solutions show a higher viscosity than the simple aqueous solution of the polymer. This change occurs with both



**FIG. 5.7** Measured flow curves for a crosslinked ASE polymer in solutions of increasing SLS concentration.



**FIG. 5.8** Measured flow curves for a HASE polymer in solutions of increasing alkyl polyglucoside (APG) concentration.



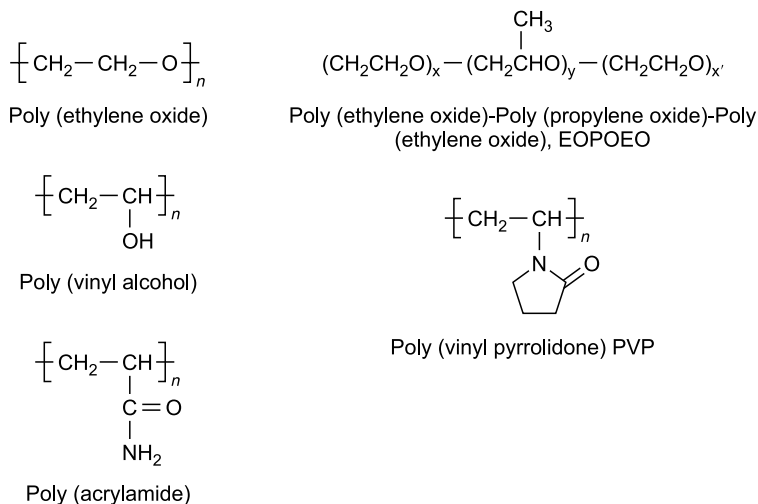
**FIG. 5.9** Measured flow curves for a HASE polymer in solutions of increasing SLS concentration.

anionic and nonionic surfactants, and is more marked with the less hydrophobic HASE rheology modifiers. As the polymer becomes more hydrophobic, either due to longer chain hydrophobes or to a greater number of hydrophobes (hydrophobe density), so this effect becomes somewhat attenuated.

The noncrosslinked ASE polymers are of interest due to their good electrolyte tolerance and their tendency to thicken formulations containing high levels of alkaline salts and builders. Thus, these types of polymer are often preferred in industrial and institutional cleaners.

## B. Synthetic Nonionic Polymers

Water-soluble synthetic nonionic polymers represent a large class of thickeners and rheology modifiers. Included in this group of commercial rheology modifiers are polymers based on polyacrylamide (pAm), polyethylene oxide or glycol (PEO or PEG), block copolymers (ethylene oxide [EO] and propylene oxide [PO]), polyvinyl alcohol (PVA), and polyvinyl pyrrolidone (PVP) (Figure 5.10). Nonionic polymers are generally compatible with anionic, nonionic, amphoteric, and cationic surfactants. They also have a much better tolerance for electrolytes than anionic polymers. Depending on the specific chemistry, nonionic polymers may exhibit a cloud point behavior, undergo base or acid hydrolysis, and may be unstable (certain types, e.g., pAm) to harsh environments such as peroxides, persulfates, or hypochlorite.



**FIG. 5.10** Representative synthetic nonionic homopolymers.

The rheological behavior of aqueous pAm solutions is typically pseudoplastic. An example of the use of pAm polymer to thicken an acidic composition is disclosed in patent application WO 9419443 A1 [16].

EO-based polymers are classified as PEGs or PEOs depending upon their molecular weight [17]. Low-to-medium-molecular-weight (200 to 25,000) homopolymers of EO are referred to as PEGs and polymers with molecular weight range of 100,000 to 2,000,000 are classified as PEOs. PEG esters, and in particular the diesters, can also be used as thickeners in surfactants. The most common of this class is the PEG-6000 distearate, which is often referred to as a hydrophobically modified nonionic polyol, or HNP. Being an ester, it has a limited pH range over which it can be used. Materials thickened with this additive tend to be relatively Newtonian in their behavior. Heat is required to incorporate the thickener, which has a melting point of about 60°C. One of the limitations with this class of thickener is that in general the higher the surfactant content, the greater the concentration of thickener required to achieve the desired viscosity. As such, they are usually encountered in formulations that contain less than about 15% surfactant. The stearic acid diester of PEG,  $(\text{PEG})_n$ -stearate ( $n = 2$  to 175), is most often used to thicken shampoos. The esters are also used as thickeners in lotions, emulsions, cream deodorants, and hair conditioners [17].

Block copolymers of EO and PO such as EO-PO-EO, which are formed by condensing EO onto polypropylene glycol, are useful rheological additives with applications in household cleaners (toilet bowl cleaners, gels for cleaning

vertical surfaces), personal care (shampoos, shaving creams, hair styling gels, antiperspirant gels, etc.), and pharmaceutical products (such as toothpastes and ointments). The viscosity build is the result of hydrogen bonding in aqueous systems, caused by the attraction of the polymer ether oxygen atoms to water protons. Alkylated EO–PO polymers are also suggested to thicken a liquid fabric softening composition [18].

Poly(*N*-vinyl-2-pyrrolidone), PVP, is available in various molecular weights (10,000, 40,000, 160,000, and 360,000) and can yield solutions of varying viscosities. PVP is best known for its unusual complexing ability toward many types of small molecules and for its physiological inertness [19]. As a thickener, it is used in biomedical, pharmaceutical, cosmetic, and personal care products (hair styling gels, shaving creams, shampoos, emollient creams and lotions, etc.).

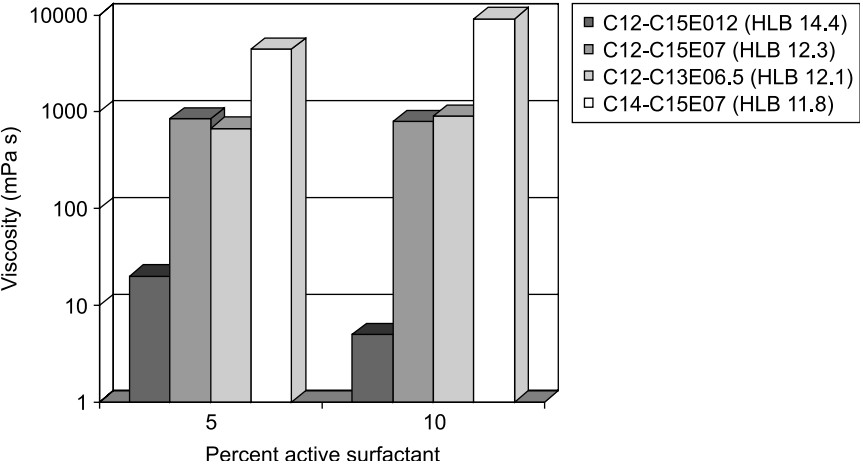
### C. Urethanes

The hydrophobically modified ethoxylated urethane (HEUR) rheology modifiers are intermediate molecular weight nonionic polymers which combine a hydrophilic backbone of varying chain length PEG with a hydrophobic, long-chain alcohol via a diisocyanurate linkage. The hydrophobicity of the long-chain alcohols can be adjusted by altering the alkyl chain length, grafting one or more hydrophobes onto the polyol chain, or attaching these hydrophobes either terminally or pendant to the polymer backbone. Due to the fact that HEUR rheology modifiers possess a relatively low molecular weight, particularly when compared to HASE polymers, thickening is achieved through the associative interaction between the hydrophobic portion of the molecule and other hydrophobic components in the formulation (surfactants, oils, pigments).

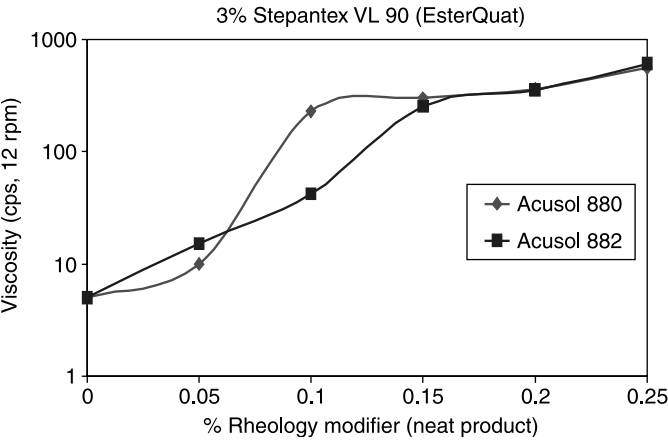
In the presence of surfactants, studies have indicated that the degree of association achieved with nonionic rheology modifiers tends to be greater when surfactants of lower hydrophilic–lipophilic balance (HLB) are employed [20,21]. This leads to significantly higher measured viscosities (using a fixed concentration of HEUR rheology modifier) with minor changes in the surfactant composition (Figure 5.11). The “size” of the surfactant hydrophobe at a given HLB also plays a role in determining the performance of these polymers, larger hydrophobes generally being preferred.

The rheology of HEUR-type polymers varies with a given formulation, but these polymers typically impart Newtonian behavior to the systems with which they are mixed, particularly at higher shear rates.

Due to the chemical nature of HEUR rheology modifiers, no neutralization is required to induce thickening. These materials are therefore compatible with anionic, nonionic, and cationic surfactant matrices, and are effective across a wide range of pH (3 to 13) [22]. HEUR rheology modifiers are used in cationic systems such as rinse-added fabric softeners (where anionic thickeners have



**FIG. 5.11** Effect of nonionic surfactant HLB on viscosity of HEUR rheology modifiers.



**FIG. 5.12** Effect of rheology modifier concentration on cationic surfactant viscosity.

incompatibility problems). The new generation of highly biodegradable cationics (esterquats) deliver extremely low viscosities at use concentrations in aqueous fabric softeners. Incorporation of very low concentrations of the appropriate HEUR thickener can generate significant viscosity build and formula stabilization, providing consumer compositions with more acceptable product aesthetics (Figure 5.12).



Another area where HEUR rheology modifiers find utility is in acidic household cleaning products (typically formulated for the bathroom or kitchen). Many of the more commonly used rheology modifiers provide thickening benefits only upon neutralization (via chain–chain entanglement), and are ineffective in these types of applications. The addition of a small amount of the appropriate surfactant and HEUR rheology modifier to a system containing citric, sulfamic, or phosphoric acid can deliver acceptable viscosity, a transparent appearance, and good overall product stability. These polymers have been used successfully to thicken peroxide bleach formulations containing up to 25% hydrogen peroxide without inducing any appreciable loss of active oxygen.

## D. Synthetic Cationic Polymers

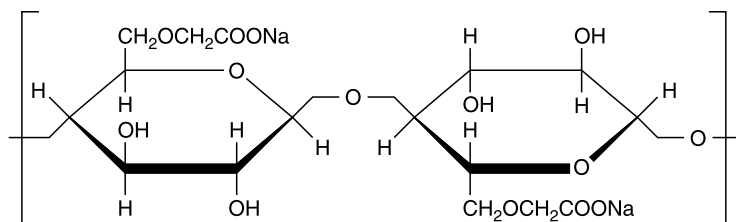
There are instances where a formulator may need to turn to cationic rheology modifiers, although these are less widely used. Synthetic cationic polymers are of three types: ammonium (primary, secondary, tertiary, and quaternary), sulfonium, and phosphonium compounds [23]. Of these, the ammonium-based polymers constitute a large class of materials with diverse applications such as additives for shampoos and soaps, as antistatic and thickening agents for rinse-added fabric softeners, in papermaking, mineral processing, and petroleum recovery, as stabilizers for emulsion polymerization, as biocides in waste water treatment, and in grease thickeners, hair sprays, and hair gels.

The copolymer of acrylamide and ammonium acrylate is used to build viscosity in rinse cycle fabric softeners. This polymer is compatible with nonionic and most cationic surfactants that are used in fabric softener formulations. The polymer is incompatible with anionic surfactants and strong oxidizing agents, and it is sensitive to electrolytes. An example of other cationic polymers useful as thickeners for aqueous acid solutions is described in patent application EP 395282 [24].

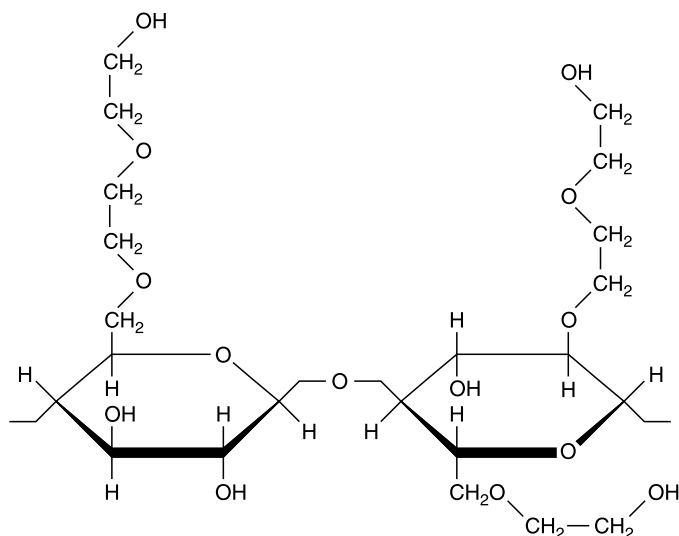
## E. Celluloses

Modified organic thickeners can be derived from naturally occurring water-insoluble polymers such as cellulose, chitin, and starch [25,26]. The most common derivatives include carboxymethyl, hydroxyethyl, hydroxypropyl, and methyl cellulose. Cationic, anionic (sulfate, phosphate), and zwitterionic derivatives have also been reported in the literature.

Sodium carboxymethyl cellulose (CMC, cellulose gum) is an anionic, water-soluble polymer (Figure 5.13). It is stable in a pH range of 4 to 10 and is compatible with most monovalent and divalent salts, as well as most anionic and nonionic materials. However, it is generally incompatible with cationic species due to its anionic nature. The structural stability of dispersions induced by CMC is highly dependent upon the concentration of the polymer. CMC is used as a thickener in toothpastes, skin creams, lotions, and food applications. The degree of



**FIG. 5.13** Idealized unit structure of CMC, with a DS of 1.0. (Reproduced with permission from Hercules Inc., Aqualon Division, Copyright 2004, Hercules Inc., Wilmington, DE.)



**FIG. 5.14** Idealized structure of hydroxyethyl cellulose. (Reproduced with permission from Hercules Inc., Aqualon Division, Copyright 2004, Hercules Inc., Wilmington, DE.)

substitution (DS) for a given CMC grade is the average number of substituted hydroxyl groups per ring. Therefore, the theoretical maximum DS is 3. The maximum substitution level of commercial CMC is a DS of 1.4. Thixotropy in CMC typically increases with decreasing DS.

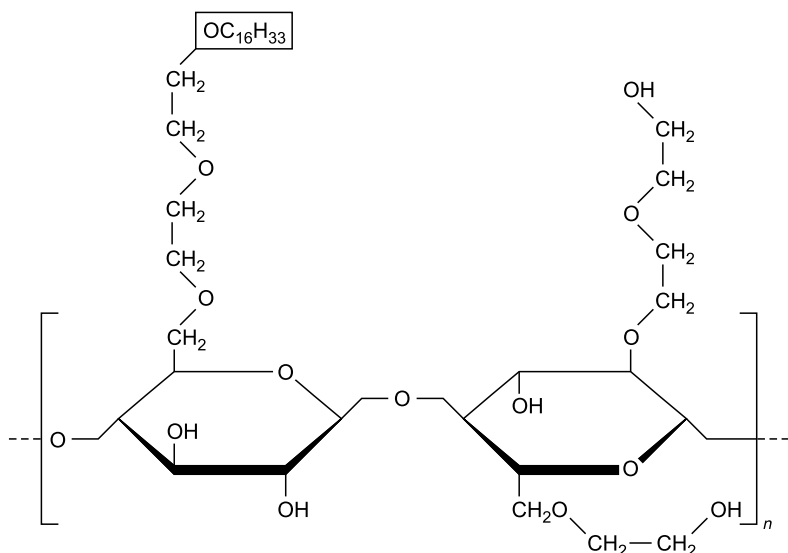
Hydroxyethyl cellulose (HEC) is a water-soluble nonionic polymer having the general structure shown in Figure 5.14 [27]. The water solubility of HEC depends upon DS and the molar substitution (MS; also termed moles of substitution).

MS is the average number of moles of substitution (in the case of HEC, hydroxyethyl and ethoxy units) added per anhydroglucose ring. The MS value, unlike DS, can exceed 3 in the case of HEC, since side chains of PEO can form. Commercial water-soluble HEC samples have DS values in the range 0.85 to 1.35 and MS values in the range 1.3 to 3.4. HEC aqueous dispersions are pseudoplastic and thermally reversible. HEC is compatible with nonionic, cationic, and anionic materials (salts and surfactants). It is stable in the pH range 2 to 11. As a thickener, it is used in hair care products (conditioners, etc.), liquid soaps, shaving products, cationic lotions, antiperspirants, and deodorants.

Hydroxypropyl methyl cellulose and methyl cellulose are also water-soluble nonionic polymers [28]. They are compatible with inorganic salts and ionic species up to a certain concentration. Methyl cellulose can be salted out of solution when the concentration of electrolytes or other dissolved materials exceeds certain limits. Hydroxypropyl methyl cellulose has a higher tolerance for salts in solution than methyl cellulose. Both are stable over a pH range of 3 to 11. Commercial water-soluble methyl cellulose products have a methoxy DS of 1.64 to 1.92. A DS of lower than 1.64 yields material with lower water solubility. The methoxy DS in hydroxypropyl methyl cellulose ranges from 1.3 to 2. The hydroxypropyl MS ranges from 0.13 to 0.82. Methyl cellulose and hydroxypropyl methyl cellulose polymers have a number of applications and are used as thickeners in latex paints, food products, shampoos, creams and lotions, and cleansing gels. U.S. Patent 5,565,421 is an example of the use of hydroxypropyl methyl cellulose polymer to gel a light-duty liquid detergent containing anionic surfactants [29].

As is the case for HASE and cross-polymers, grafting of long-chain alkyl hydrophobes onto water-soluble cellulosic polymers leads to modified solution properties such as enhanced viscosity, surface activity, and unusual rheological properties [30–35]. Associative cellulosic thickeners build viscosity through two mechanisms: hydrogen bonding with water molecules (as with the unmodified cellulosic polymers) and micellar interactions that occur between the hydrophobic groups. The hydrophobic association can be viewed as pseudo-crosslinks which induce a three-dimensional network. The hydrophobic groups on the polymer can also interact more favorably with surfactant micelles to build viscosity in dispersions. The enhanced solution viscosity of C16 hydrophobically modified HEC is the result of intermolecular associations via the hydrophobic groups (Figure 5.15). Primary applications, sensitivity to electrolytes, and pH stability of this hydrophobically modified polymer are similar to those of unmodified HEC.

A polymeric quaternary ammonium salt of HEC, polyquaternium-24, in combination with certain primary surfactants, salts, and other viscosifying agents can be used as a thickener in personal care products such as shampoos, hair conditioners, creams, and aftershave gels.

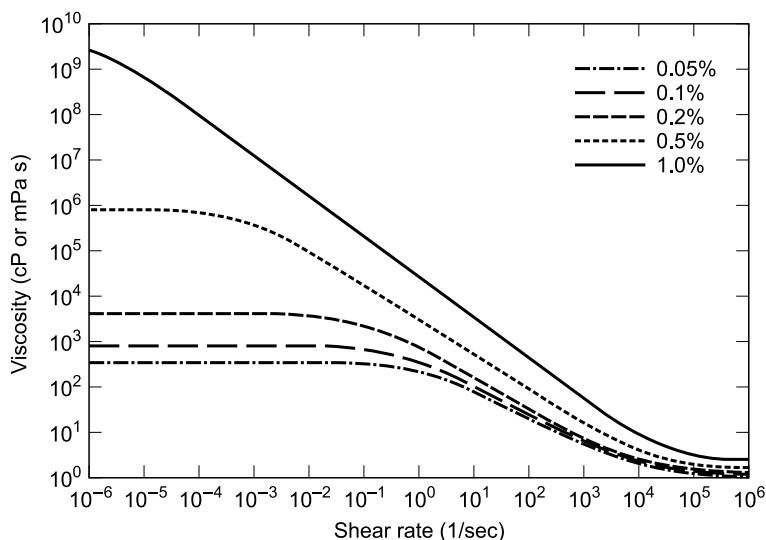


**FIG. 5.15** Idealized structure of hydrophobically modified HEC, with hydroxyethyl MS = 2.5. (Reproduced with permission from Hercules Inc., Aqualon Division, Copyright 2004, Hercules Inc., Wilmington, DE.)

## F. Gums

Several natural biopolymers originally developed for use in the food industry, including xanthan, gum arabic, carrageenan, succinoglycan, gellan, locust bean gum, and alginates, have found use recently in the detergents industry. From a commercial point of view the most significant of these today is xanthan, a water-soluble polymer based on an anionic heteropolysaccharide, and produced by bacterial fermentation, followed by recovery of the resulting exopolymer. The organism employed during the fermentation process is a species of the bacterium *Xanthomonas campestris*. The polymer, due to its nature, is biodegradable, and it is necessary to ensure that formulations using this thickener are adequately preserved to prevent bacterial spoilage from taking place over the life of the product.

Xanthan is a slightly hygroscopic powder that requires hydrating prior to use. As a consequence, it is generally introduced into the water being used to prepare the formulation at the beginning of the processing, and stirred well to disperse completely and hydrate prior to addition of the remaining components. The behavior of xanthan is extremely pseudoplastic, with very high viscosities being developed under conditions of low shear, as shown in Figure 5.16. As shear is removed, the solution rebuilds structure almost instantaneously. Xanthan is thus a good



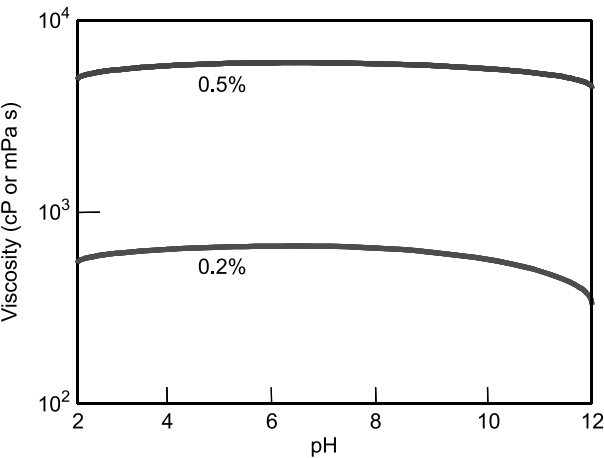
**FIG. 5.16** Flow curves for aqueous solutions of xanthan gum at various concentrations. (Reproduced with permission from CP Kelco ApS, Copyright 2004, CP Kelco, San Diego, CA.)

candidate for providing suspending properties to formulations, as well as giving vertical cling properties. Slight turbidity is often observed in finished products.

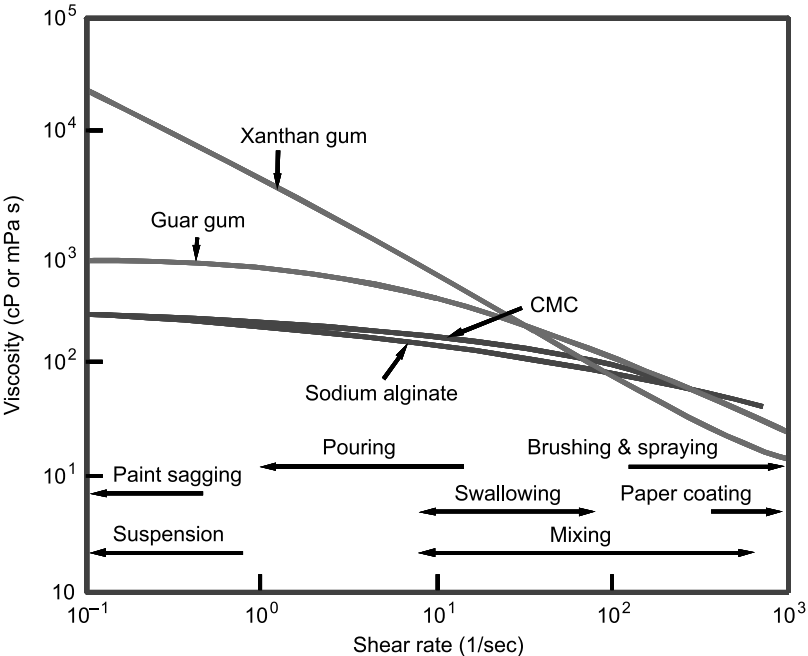
Xanthan gum is one of the few rheology modifiers stable over a wide range of pH, including both acidic and alkaline ranges (Figure 5.17). It is thus suitable for acid cleaners and scale removers as well as the traditionally neutral detergents and alkaline hard surface cleaners. Xanthan gum can be quite tolerant of both monovalent and divalent metal salts, but the presence of trivalent metal ions ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cr}^{3+}$ ) often leads to marked crosslinking, in some cases causing precipitation. Sequestering such ions will ensure stability.

Figure 5.18 shows the viscosities of some common natural polymers over a range of shear rates. At low shear rates, solutions of xanthan gum have approximately 15 times the viscosity of guar gum and an even higher margin over the viscosity of CMC and sodium alginate. This further explains the strength of xanthan gum as a stabilizer for suspensions and for providing vertical cling.

We have already mentioned that xanthan gum solutions are tolerant to both acids and bases. Solutions of xanthan gum also have excellent compatibility with many surfactants, water-miscible solvents, and other thickeners. As an anionic polysaccharide, xanthan gum is most stable with anionic surfactants (up to 20% active), nonionic surfactants (up to 40% active), and amphoteric surfactants (up to



**FIG. 5.17** Viscosity as a function of pH for xanthan gum solutions at 0.2 and 0.5% solids. (Reproduced with permission from CP Kelco ApS, Copyright 2004, CP Kelco, San Diego, CA.)



**FIG. 5.18** Flow curves of various natural polymers. (Reproduced with permission from CP Kelco ApS, Copyright 2004, CP Kelco, San Diego, CA.)

25% active) depending upon the composition of the surfactant. Generally, xanthan gum is not recommended for use with cationic surfactants, bleach solutions, and strong reducing environments.

Although encountered less frequently than xanthan, carrageenan is another of the gums sometimes used in liquid detergents. This polysaccharide is extracted from certain varieties of red seaweed [36]. The polysaccharide is made up of repeating galactose units and 3,6-anhydrogalactose, both sulfated and nonsulfated, joined by alternating  $\alpha$ 1-3 and  $\beta$ 1-4 glycosidic linkages, and is available as the kappa, iota, or lambda forms, with varying sulfate galactose ratios (1:2, 2:2, and 3:2 for the three versions, respectively). The lambda type is the most soluble and dissolves in cold water. The kappa and iota types of carrageenan form thermally reversible gels at low concentrations (1% by weight). Both kappa and iota types also form strong gels in the presence of specific ions ( $K^+$ ,  $Rb^+$ , and  $Ca^{2+}$ ) [37]. The carrageenans are stable in the pH range 3.5 to 9, with all three types undergoing hydrolysis at pH < 3.5. Carrageenans are used in toothpastes, skin creams, lotions, and food products (such as puddings, chocolate milk, and ice cream). One of the potential drawbacks is the fact that carrageenan systems have the tendency to show syneresis.

Alginates are extracted from brown seaweed, and can be thickeners or gellifiers depending on the type of alginate and the matrix. They have various conformations depending on the source of the seaweed. In the alginic acid form or as the Ca salt they have very low solubilities, but the Na or K salts are soluble. The Mg salt is the only soluble divalent salt. Even hard water will cause thickening of alginates, but the process can be controlled by the use of complexants and chelatants. Alginates show rheology much closer to Newtonian than most of the other gums.

Locust bean gum can be extracted from the European carob tree. As the extract, with impurities removed, it gives clear solutions. It shows significant synergy with carrageenan and xanthan, usually at about 50/50 levels, and this synergy tends to eliminate the syneresis often seen with carrageenan. Being insoluble in cold water, heat is required to obtain solutions.

Guar gum has a major processing advantage in that it is soluble in cold water. However, it is very much less pseudoplastic than xanthan and tends to give formulations with a long or "stringy" rheology.

#### IV. INORGANIC THICKENERS

The two most commonly used inorganic additives for rheology modification of liquid detergents are salts and smectite clays. Other inorganics such as silica and alumina have found more limited use in detergent cleaners. Each of these additive types has a distinctly different mechanism for modifying the rheology of a detergent, and very critical sensitivities within a formulation.

## A. Inorganic Salts

Perhaps the greatest benefit of using inorganic salts to thicken a system is the low cost it adds to a formulation. It is not solely salt addition that drives thickening in a detergent, but rather the interaction that the salt has with other components of the system, most notably charged (anionic and cationic) surfactants. It is this interaction between salt and surfactant of which formulators typically attempt to take advantage, and this strategy works best in detergents with relatively high surfactant levels. Liquid laundry detergents, hand dishwashing (light-duty) liquids, and hand soaps are common examples of products thickened by simple salt addition.

However, the ability to thicken surfactant systems with salt addition is not universal, even in products with relatively high levels of surfactant. Not all anionic surfactants respond to added salt with increased viscosity, but the more commonly used alkylbenzene sulfonates (ABSs) and alkyl ether sulfates (AESs) do. In particular for AESs the shorter the EO segment, the more sensitive they are to salt addition, with the alkyl sulfate (no EO) at the most responsive extreme. The ABSs can be thickened with salt addition as well, but only over a narrow viscosity range before they salt out of solution. Addition of certain nonionics, especially alkyl polyglucosides (APGs) or alkanolamides, can enhance the thickening effect in anionic surfactants, often reducing the amount of salt needed to achieve a given viscosity.

Fundamental studies of salt effects on well-characterized anionic and cationic surfactant solutions have provided a mechanistic picture that links the surfactant structures and the rheology. In [Chapter 4](#), rheology modification by neat surfactant solutions was detailed. This rheology is a complex result of, among other things, surfactant type(s) and concentration, mixture ratios, pH, and added solvents, all of which determine the structure of the surfactant aggregates, directly affecting the solution viscosity. Addition of salt provides another way of changing how surfactants develop structure. For example, Rybicki [38] showed decreasing viscosity of low-concentration sodium dodecylbenzene sulfonate solutions with addition of many different salts, while Wang [39] showed increased viscosity at higher surfactant concentration. In the former case, the salt is believed to screen the electrostatic field on the spherical micelle surface, reducing the effective volume of the micelle and thus the relative viscosity. In the latter case, the added salt drives a structural change from spherical to elongated, asymmetric micelles. The magnitude of the viscosity increase has also been observed to be dependent on the type of salt, and especially the type of counterion that is chosen (e.g.,  $\text{Na}^+$  vs.  $\text{Li}^+$  vs.  $\text{Mg}^{2+}$ ). Additionally, Gamboa and Sepulveda [40] have shown NaCl can increase the viscosity of anionic sodium dodecyl sulfate solutions and cationic cetyltrimethylammonium bromide solutions.



There are a number of potential downsides of this thickening technique. A formulator usually can control the viscosity only within a limited range, and often there is no added control over the shape of the flow curve. That is, a Newtonian product will remain Newtonian in flow rather than building in rheological features such as pseudoplasticity, thixotropy, or yield stresses. These are not restrictive limitations if one is only attempting to provide a little “body” to a formulation through small viscosity increases, but it is unlikely that salt will provide properties such as suspendability or vertical cling. Also, inorganic salts may interact negatively with other formulation components (e.g., electrolytes), resulting in a cloudy, or in the worst case unstable, product. Salts can promote irritation and possibly create corrosive conditions at high use levels. Finally, seemingly small differences in the byproducts that are formed during the surfactant synthesis can affect the salt thickening profile, resulting in potential for product variations if one does not use good process control.

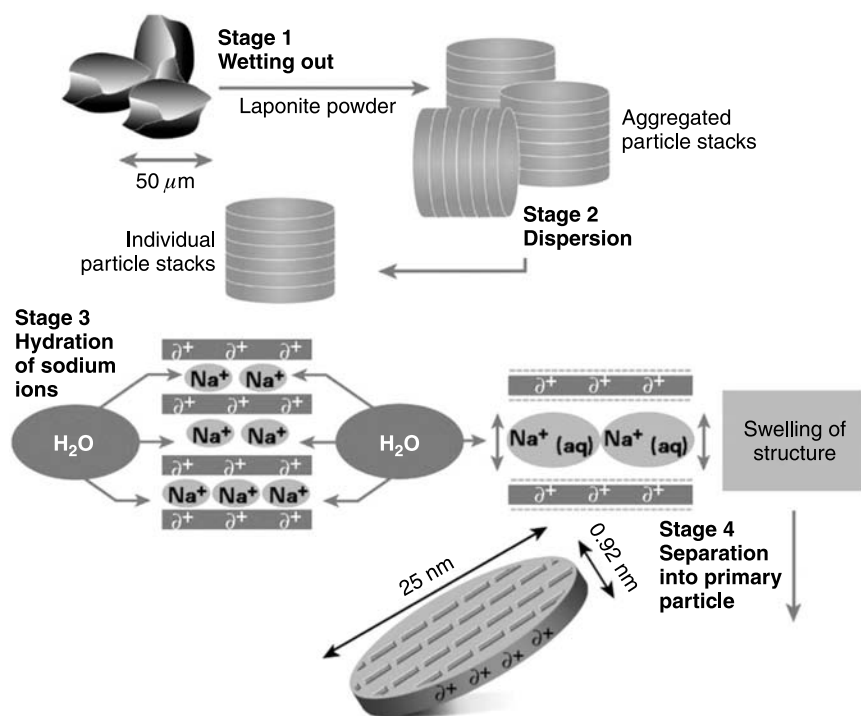
## **B. Inorganic Clays**

Smectite clays are naturally occurring water-swellable clays. Often, one finds the terms smectite, bentonite, hectorite, saponite, montmorillonite, and magnesium aluminum silicate (MAS) clays used interchangeably, leading to the potential for confusion. For clarity, smectite is the name of the subgroup of clays that encompass hectorite, saponite, and montmorillonite. Bentonite is the geological term commonly used to refer to smectite clays, the latter being a mineralogical term. The differences between hectorite, saponite, and montmorillonite clays lie in their chemical makeup and structure, with the latter two having MAS compositions [41]. All of the natural clays are mined and purified for use, typically being sold in powder form that requires a hydration step. The extent of purification of these clays can have an impact on the efficiency, clarity, and cost. The synthetic hectorite clays such as Laponite (Southern Clay Products) are typically sold as powders and similarly require hydration prior to use, but they are prepared free from impurities.

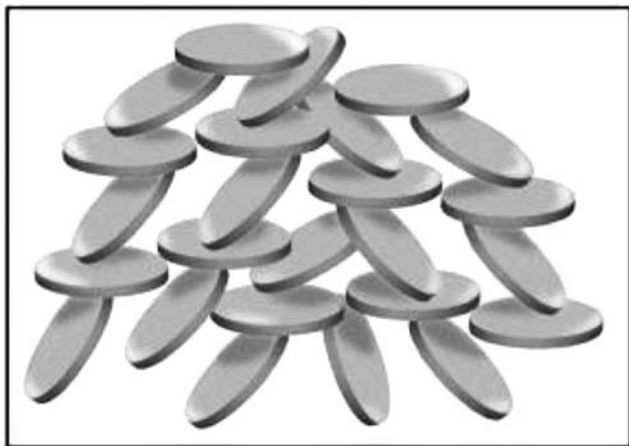
Both natural and synthetic clays are used as rheology modifiers for liquid detergents. They can stabilize emulsions and provide excellent particle suspension via the development of yield stresses. They can tolerate significant levels of water-miscible cosolvents like glycols and glycol ethers, thus finding greatest usage in surface cleaners of various types (e.g., toilet and oven cleaners). They are some of the few rheology modifiers stable to hypochlorite, and they can be formulated in products covering a wide pH range (roughly 3 to 12, but can be as low as 1), although they are not compatible with cationic species. Since these materials function via electrostatic interactions, the rheology modification they impart is

essentially temperature-insensitive, and their mineral nature makes them resistant to biological degradation. After inorganic salts, natural clays tend to be the least expensive of the rheology modifiers, although the purification steps result in higher costs than less purified materials. The synthetic hectorites are the most expensive on a per weight basis, but they also tend to be significantly more efficient than the natural clays, resulting in potential for lower use levels in formulations. Additionally, these synthetic clays can form clear, aqueous solutions due to their small particle dimensions.

The hydration step of inorganic clays is vital to their effective usage in liquid formulations. In powdered form, all smectite clays (including the synthetic analogs) exist as aggregates of stacks of primary, disk-like clay platelets. When stirred in water, these aggregates break up toward the individual stacks, which can then hydrate, swell, and delaminate to the primary clay particle. This is shown schematically for the Laponite example in Figure 5.19. Energetic mixing and



**FIG. 5.19** Schematic of the wetting and delamination of inorganic clay particles. (Supplied by and used with the permission of Southern Clay Products.)



**FIG. 5.20** Schematic of the “house-of-cards” structure derived from clay platelet edge-face interactions. (Supplied by and used with the permission of Southern Clay Products.)

sufficient free water is required for full hydration of the particles and for full effectiveness to be achieved. Completely delaminated, each primary clay particle has a thickness typically of the order of 1 to 3 nm with face dimension dependent on clay type, ranging from about 25 to 1000 nm. The flat, larger face holds an anionic charge, while the thin outer edge of the plate is slightly positive. At sufficient concentration, the clay particles align and fill space in what is known as a house-of-cards structure, with the positive edges of one particle interacting with the negatively charged face of another, as shown in Figure 5.20. This stacking provides structure in the aqueous system resulting in the creation of a yield stress.

These clays are unique in the fact that although they can build yield structures, they typically do not provide significant thickening. Once sufficient shear is applied to break the three-dimensional structure, the small clay particles provide minimal resistance, and thus the viscosity decreases to essentially that of the clay-free system. (This is one reason clays are usually used in conjunction with co-thickeners.) Once the fluid is brought again to rest, the clay platelets reorient and rebuild the yield stress. The yield value achieved and the time it takes to rebuild after breakdown are dependent on clay concentration and can be low and slow at low usage levels. Thus, clay-modified systems are examples of thixotropic, highly pseudoplastic, or yield-containing solutions. The result can be readily pourable systems that maintain a stable suspension or provide a degree of wall cling after spraying.

As described above, the ability of smectite clays to act as rheology modifiers is a result of their interparticle electrostatic interactions. Thus, their behavior and

stability are very sensitive to relatively low levels of electrolyte in a formulation. For example, Mourchid and co-workers [42] have studied the phase behavior and stability of aqueous Laponite solutions in the presence of NaCl. For solutions above roughly 0.01 M, they find a flocculated clay state, independent of the concentration of the clay. In clay-modified detergent formulations such flocculation can lead to syneresis and instability, as well as increased opacity.

It is commonly recommended to utilize a second rheology modifier along with smectite clays in order to increase formulation stability and/or to provide more precise control to the overall rheology. Often, synergistic rheology is observed in these blends, resulting in viscosity increases greater than what would be expected based on the behavior of the two individual modifiers. This can lead to utilization of lower levels of each thickener, reducing total formulation cost and potentially eliminating some of the drawbacks of using the higher level of the co-thickener. Recommended co-thickeners include organic gums such as xanthan gum, cellulose derivatives such as CMC and HEC, and polyacrylics such as HASE and carbomer polymers.

## V. SUMMARY

There are many distinct types of rheology modifiers to which a formulator can turn so as to achieve the flow characteristics necessary for a liquid detergent formulation. Deciding where to start, or even who to contact for help, can be complicated even more by the numerous unique “flavors” that are available within each larger class of modifier. Initially, one can try to narrow the choices based on some general aspects of the formulation, such as pH or salt level. [Table 5.3](#) provides a summary of each of the technology classes discussed in this chapter, their broad applicability under various formulation conditions, and some handling considerations.

It is clear that some classes of rheology modifiers will have more utility in certain detergent systems than in others. For example, the subset of modifiers that function in the neutral-to-alkaline range of pH would not be suitable for an acid-based surface cleaner at very low pH. [Table 5.4](#) provides some guidance for choosing a rheology modifier based on different detergent applications.

These summary tables, along with the accompanying discussion throughout the chapter, provide formulators with much of the background knowledge needed to make an educated initial choice of rheology modifier for their specific formulation needs. However, with the on-going growth of liquid detergents in the consumer market, there is a corresponding need to differentiate these products to the consumer. Formulations will get more intricate, the demands on the rheology modifier system will become more complex, and the current stable of modifiers may not meet these demands. Solutions to these requirements may come from unique mixtures of available modifiers, or they may come from newly developed chemistries within the various classes of rheology modifiers. As many of the companies that

**TABLE 5.3** Summary of the Applicability of Various Rheology Modifiers, with their Common As-Supplied Formats

Class	Electrolyte tolerance	pH range	Pseudoplasticity	Neutralization required	Typical form of raw material
ASE (crosslinked)	Moderate	Neutral to alkaline	High	Yes	Liquid
ASE (noncrosslinked)	Excellent	Neutral to alkaline	Low	Yes	Liquid
Carbomers	Poor	Neutral to alkaline	High	Yes	Powder
Cellulosics (ionic)	Poor	Neutral to alkaline	Medium	Yes	Powder
Cellulosics (nonionic)	Excellent	Acidic to alkaline	Medium	No	Powder
Cross-polymers	Poor	Neutral to alkaline	High	Yes	Powder
HASE	Good	Neutral to alkaline	High	Yes	Liquid
HEUR	Good	Acidic to alkaline	Low	No	Liquid
Synthetic nonionics/HNP	Moderate	Acidic to alkaline	Low	No	Powder
Inorganic clays	Poor	Acidic to alkaline	Very high	No	Powder
Xanthan	Good	Acidic to alkaline	High	No	Powder

**TABLE 5.4** Summary of Preferred Rheology Modifiers by Application

	ASE	HASE	Carbomer/ cross- polymers	HEUR	Xanthan	Inorganic clays	Cellulosics	Synthetic nonionics/ HNP	Salts
Hand dishwashing	+	+					+	+	+
Laundry		+			+				
Auto dishwashing									
Chlorinated			+						
Nonchlorinated	+		+						
Hand soap		+			+			+	+
Surface cleaners									
Acidic				+	+	+			
Alkaline	+	+	+			+			
Peroxide			+	+		+			
Hypochlorite			+			+			
Fabric softeners				+					
Shampoos/conditioners	+	+				+	+	+	+

offer rheology modifiers have active development programs, formulators should be encouraged to contact the technical staff of these suppliers for further specific guidance for individual formulation needs.

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