

Guar Gum and Its Derivatives Interact with Different Surfactants

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Abstract

Investigations were used to show the interaction between galactomannans, guar gum (GG), and sodium lauryl ether sulphate (SLES). At a crucial aggregation concentration, SLES and GG formed aggregates and decreased the surface tension. Since no aggregation was seen in conductometric, tensiometric, or pyrene probe tests using the non-ethoxylated version of sodium lauryl sulphate, or SLS, the interaction was attributed to the presence of surfactant ethoxyl (EO) groups. According to the dynamic light scattering study (DLS), the aggregates produced between SLES and GG showed a size of roughly 26 nm and a negative zeta potential, indicating that the polymer is surrounded by SLES. The aggregation happens spontaneously and is a driven-enthalpy and driven-entropy process, as demonstrated by the determination of the thermodynamic parameters. Using regularly used thickeners like GG, the interaction between SLES and GG might be investigated to create formulations with lower quantities of surfactants.

Key Words: Sodium lauryl ether sulphate (SLES), Guar gum (GG), Surfactants

1. Introduction

Guar gum, additionally called guaran, is a galactomannan polysaccharide removed from guar beans that has thickening and settling properties valuable in food, feed, and modern applications. The guar seeds are precisely dehusked, hydrated, processed and screened by application. It is normally delivered as a free-streaming, grayish powder. Guar gum is made from the seeds of the Leguminosae family plant *Cyamopsis tetragonoloba*, a drought-tolerant species [1]. The common names for guar gum flour, beans, and galactomannan fractions in scientific literature are guar, Indian cluster beans, and guaran, respectively. A type of polysaccharide known as galactomannans has a mannose backbone and galactose side groups. A chain of (1-4) beta-D-mannopyranosyl units makes up the primary backbone, which is connected to a single unit of (1-6) alpha-D-galactopyranosyl. $1.2-2.0 \times 10^6$ g/mol is weight of polymer varied. Guar gum structure explained by fig.1. Here 2 mannose unit and 1 galactose unit are shown.

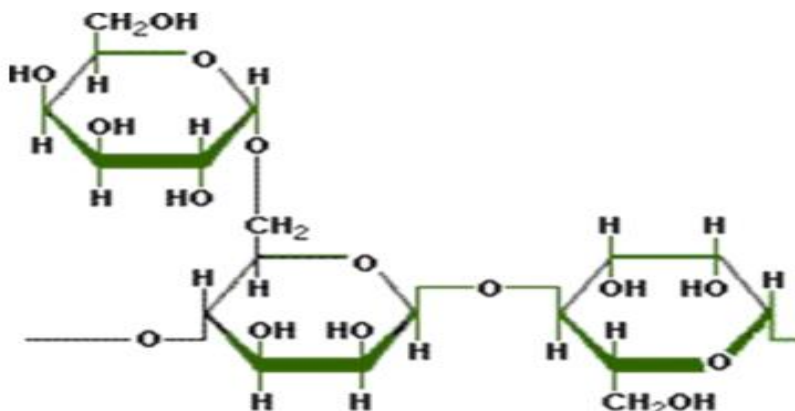


Figure 1. Structure of guar gum polymer

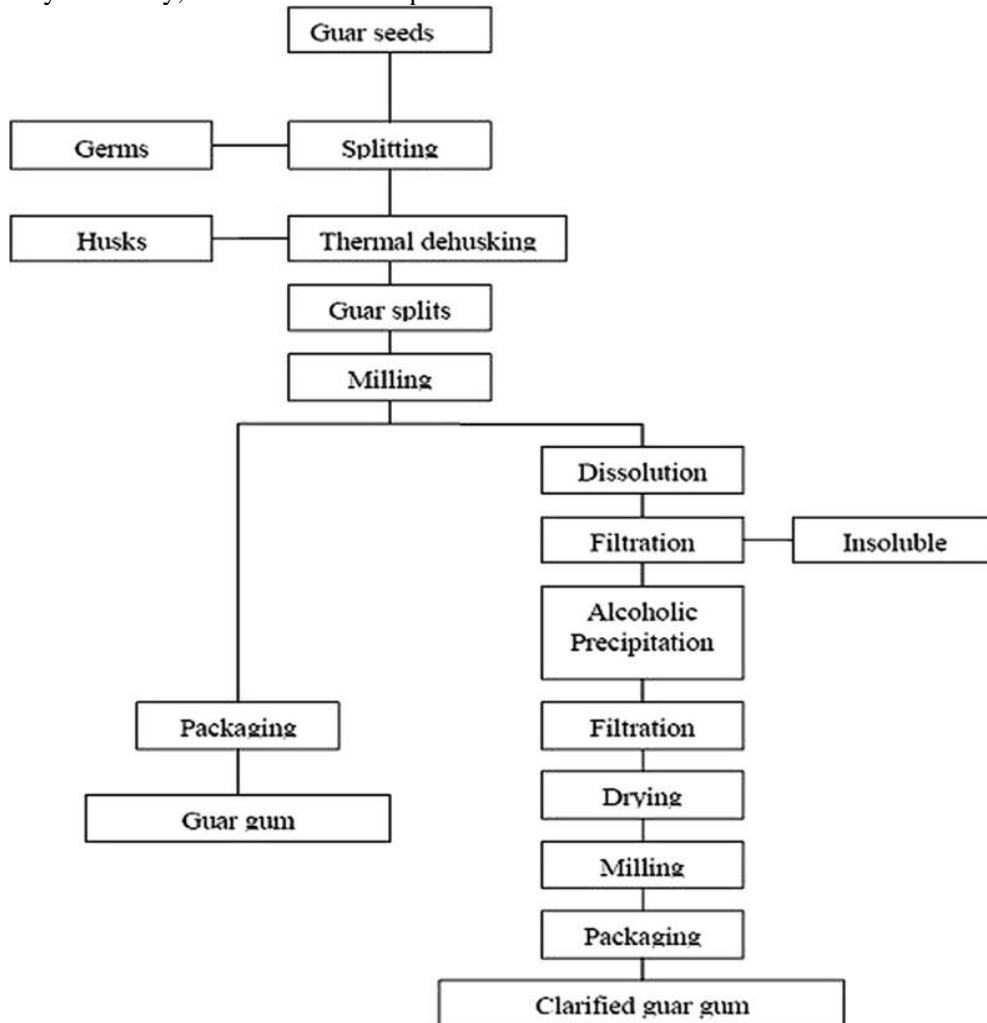
Guar gum is dissolved by water thus it's ratio mannose to galactose changes (1.2 to 1.8) In solution with other material the dipolar ion dipolar and hydrogen bonding is because of they have plenty of oxygen, hydroxyl center and carboxylate center Thus, it is chief to use as stabilizer and thickener.

Production and trade: -

The guar bean is mainly filled in India, Pakistan, the United States, Australia and Africa. India produces around 2.5-3 million tons of guar yearly, making it the biggest maker, with around 65% of world creation. In India, Rajasthan, Gujarat and Haryana are the principle creating areas. The US has delivered 4,600 to 14,000 tons of guar throughout the most recent 5 years. Texas land beginning around 1999 has varied from around 7,000 to 50,000 sections of land. The world creation for guar gum and its subordinates is around 1.0 million tons. Non-food guar gum represents around 40% of the complete interest.

Processing: -

Guar gum handling changes from one plant to another. The overall layout of the assembling system of guar gum is displayed in Fig. 1. At the point when guar seeds are eliminated from their pods these are circular in shape, earthy in variety, more modest than pea seeds in size.



The gum is financially removed from seeds basically by a mechanical course of broiling, differential wearing down, sieving and cleaning. The seeds are broken and the microbe is isolated from the endosperm.

Two parts of the endosperm are gotten from each seed and are known as unhusked guar split. At the point when the fine layer of stringy material, which shapes the husk, is taken out and isolated from the endosperm parts by cleaning, refined guar parts are acquired. The frame (husk) and microorganism piece of guar seed are named as guar feast which is a significant result of guar gum powder handling and is used as dairy cattle feed. The refined guar parts are then treated and completed into powders (known as guar gum) by an assortment of courses and handling methods relying on the final result wanted. The pre hydrated guar parts are squashed in flicker factory and afterward consistently moved to ultrafine processor, which crushes the parts without creating an excess of hotness.

The crushed material is dried and gone through evaluates for reviewing of the material as indicated by the molecule size. Different grades are accessible relying on variety, network size, consistency potential and pace of hydration [2]. In modern handling of guar gum expulsion is additionally included before hydration and chipping. After these means crushing and drying are finished. Consideration of expulsion gives guar gum powder with further developed hydration rate [3]. The results of guar gum industry are Churi and Korma which are used for dairy cattle feed.

Non-food applications

Request of guar gum has expanded during most recent couple of a long time because of the advancement of various subordinators of guar gum like anionic and cationic subsidiaries. Present business significance of guar gum is a direct result of its utilization in oil and gas well feeling explicitly water powered breaking in which high strain is utilized to break rock. Guar gum makes the cracking liquid thicker with the goal that it can convey sand into broke rock. This break stays open because of presence of sand which makes a way for gas or oil to stream to all around bore. Guar subsidiaries for use in cracking liquids are hydroxypropyl guar (HPG) and carboxymethyl hydroxypropyl guar (CMHPG). Guar gum has been utilized in explosives for more than 25 years as an added substance to explosive for water hindering. Lately, it has turned into the essential gelling specialist in water based slurry explosives. Water impeding, enlarging and gelling property of guar gum make it empower to use as an added substance in dangerous industry. Touchy property is kept up with by blending of ammonium nitrate, nitroglycerine and oil explosives with guar gum even in wet circumstances. The development of paper is improved by an expansion of modest quantities of guar gum to the mash. It fills in as a fiber deflocculent and dry-strength added substance. It gives denser surface to the paper utilized in printing.

Research examination shows that high thickness guar gum subsidiaries can be gotten by treatment of guar gum with complexing specialists like natural titanates, chromium salts and aluminum salts. These specialists respond with guar gum to frame buildings with high consistency gel.

Composition and Structure

The guar bit is made out of a few layers, to be specific the external husk (16-18%), the microorganism (43-46%) and the endosperm (34-40%). The microorganism part of its seed is prevalently protein and the endosperm dominantly galactomannan. Guar gum essentially comprises of the great sub-atomic weight polysaccharides of galactomannans which are direct chain of (1→4) connected β -D-mannopyranosyl units with (1→6) connected α -D-galactopyranosyl deposits as side chains as displayed in Fig. 2. These galactose and mannose bunches establish the galactomannan part of seed endosperm. It was first accepted that the sidegroups were subbed at standard stretches along the mannan spine [4]. Nonetheless, test utilizing protein debasement of guar [5], spectroscopic techniques [6] and programmatic experience show more arbitrary dissemination of galactose side gatherings as given in Fig. 3.

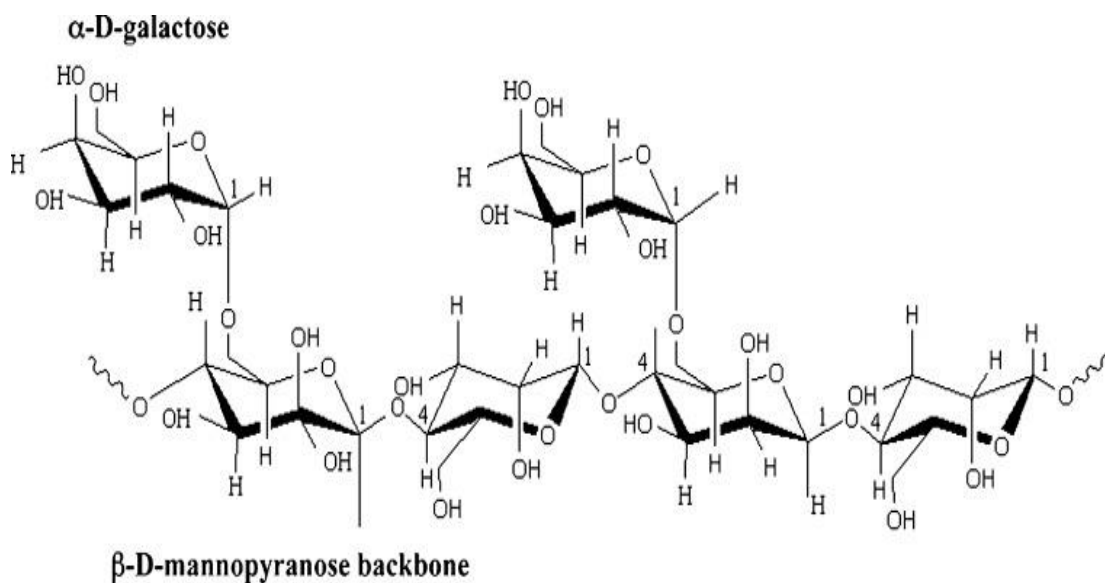
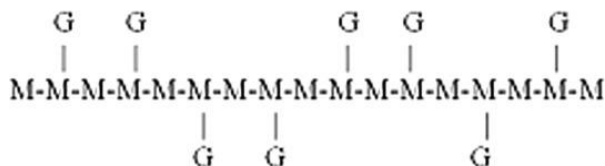


Fig-2

Regular Distribution



Random Distribution

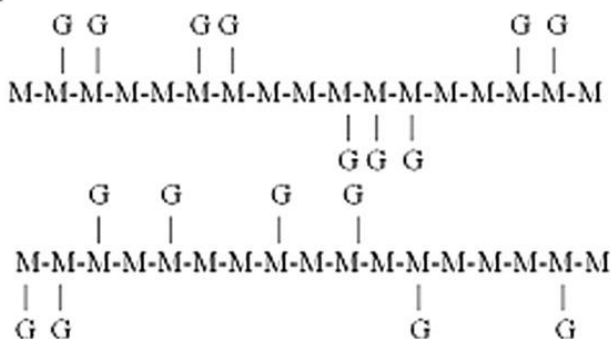


Fig-3 Arbitrary dissemination of galactose side gatherings

One such model proposes a guar galactomannan in which the galactosyl units are haphazardly organized for the most part two by two and trios [7]. The proportion of mannose to galactose units has generally been accounted for as 2:1 [8]. Different examination concentrates on help proportions in the scope of 1.6:1 to 1.8:1. Current information likewise recommend that galactomannans from various guar assortments have a similar galactose/mannose plan [5]. The more noteworthy expanding of guar is accepted to be liable for its simpler hydration properties as well as its more prominent hydrogen holding action. It is likewise announced that totals are unmistakable in guar frameworks and may play significant part in viscoelastic way of behaving of arrangement, contingent upon how they are interlinked [9]. Guar is a polysaccharide with one of the greatest sub-atomic loads of all normally happening water solvent polymers. The viscosifying impact of business guar gum arrangements can shift gigantically relying upon the atomic load

of the galactomannan. Early distributions revealed that normal atomic load of guar gum change gigantically, contingent upon what strategy is utilized, yet these are ordinarily in the scope of 0.25-5.0 million. Outright strategies have likewise been utilized to decide sub-atomic weight, including light dissipating methods, which are additionally valuable for giving underlying data on the polysaccharide [10-13].

Properties: -

Chemical composition

Synthetically, guar gum is an exo-polysaccharide made out of the sugars galactose and mannose [14]. The spine is a direct chain of β 1,4-connected mannose buildups to which galactose deposits are 1,6-connected at consistently mannose, shaping short side-branches. Guar gum can endure temperatures of 80 °C (176 °F) for five minutes.

Solubility and viscosity

Guar gum is more dissolvable than insect bean gum because of its additional galactose branch focuses. Not at all like grasshopper bean gum, it isn't self-gelling. Either borax or calcium can cross-connect guar gum, making it gel. In water, it is nonionic and hydrocolloidal. It isn't impacted by ionic strength or pH, however will corrupt at outrageous pH and temperature (for example pH 3 at 50 °C). It stays stable in arrangement over pH range 5-7. Solid acids cause hydrolysis and loss of consistency and alkalies in solid focus additionally will more often than not decrease thickness. It is insoluble in most hydrocarbon solvents. The consistency achieved is subject to time, temperature, fixation, pH, pace of tumult and molecule size of the powdered gum utilized. The lower the temperature, the lower the rate at which consistency increments, and the lower the last thickness. Above 80°, the last thickness is somewhat diminished. Better guar powders grow more quickly than bigger molecule size coarse powdered gum. Guar gum shows a reasonable low shear level on the stream bend and is unequivocally shear-diminishing. The rheology of guar gum is normal for an irregular loop polymer. It doesn't show the exceptionally high low shear level viscosities seen with more inflexible polymer chains, for example, thickener. It is very thixotropic above 1% focus, however beneath 0.3%, the thixotropy is slight. Guar gum shows thickness cooperative energy with thickener.

Thickening:

One utilization of guar gum is a thickening specialist in food sources and meds for people and creatures. Since it is without gluten, it is utilized as an added substance to supplant wheat flour in heated goods 9:41. It has been displayed to lessen serum cholesterol and lower blood glucose levels. Guar gum is likewise conservative since it has just multiple times the water-thickening capacity of different specialists (for example cornstarch) and just a little amount is required for delivering adequate thickness. Since less is required, costs are diminished. Notwithstanding guar gum's consequences for consistency, its high capacity to stream, or disfigure, gives it ideal rheological properties. It structures fragile gels when cross-connected with boron. It is utilized in different multi-stage details for water driven breaking, in some as an emulsifier since it keeps oil drops from coalescing and in others as a stabilizer to assist with keeping strong particles from settling as well as isolating. Deep earth drilling involves the siphoning of sand-loaded liquids into an oil or flammable gas repository at high tension and stream rate. This breaks the supply rock and afterward props the airs out. Only water is too dainty to be in any way powerful at conveying proppant sand, so guar gum is one of the fixings added to thicken the slurry combination and work on its capacity to convey proppant. There are a few properties which are significant. Thixotropic: the liquid ought to be thixotropic, meaning it ought to get inside a couple of hours. The ideal thickness shifts over the direction of a couple of hours.

Grading: Table 1- General arrangement of guar gum

Guar gum is analysed for

Test	Test Method	Test	Test method
Colour	09	Acid-insoluble residue	115
Viscosity	10/04	Fat content	18
Granulation (mesh)	21	Ash content	12
Moisture, pH	1 and 29	Gum content	03
Protein	05	Heavy metals	13
Insolubles Ash	11	Filterability	20A

Industrial applications:

- Material industry - measuring, getting done and printing
- Paper industry - further developed sheet arrangement, collapsing and denser surface for printing
- Explosives industry - as waterproofing specialist blended in with ammonium nitrate, dynamite, and so forth.
- Drug industry - as folio or as disintegrator in tablets; primary fixing in some mass shaping purgatives
- Beauty care products and toiletries businesses - thickener in toothpastes, conditioner in shampoos (for the most part in an artificially adjusted rendition)
- Water powered cracking Shale oil and gas extraction businesses polishes off around 90% of guar gum delivered from India and Pakistan.

Derivatives of guar gum:

Guar gum derivatives are created by substituting various reactive functional groups for the macromolecular backbone and reactive hydrogen from free hydroxyl groups [15]. This alteration is established not-exclusively to beat its intrinsic challenges, for example, the thickness decrease because of uncontrolled pace of hydration, turbidity in aqueous dispersion, solubility based on PH and high powerlessness to microbial assault yet in addition to limits its drawn out application and furthermore helps in enhancement of its general characteristics and solubility [16] Therefore synthetic alteration of GG expands its viewpoint in various applications under the chemical modification, for example, in oil field, food, mining, paint and pigment, paper, personal care, water treatment, pharmaceutical and new kinds of superabsorbent [17] It further includes hydroxyl groups cross linking reaction, etherification and esterification.

Lists of some derivatives of guar gum are shown below:

- I. O-carboxymethyl- O-hydroxypropyl GG (CMHPG)
- II. Hydroxymethyl GG [18]
- III. Methacryloyl GG
- IV. Carboxymethyl GG
- V. Esters of GG VI.
- VI. Acryloyloxy GG [19]
- VII. O-carboxymethyl-O-2 hydroxy-3-(trimethylammonia propyl) GG (CMHTPG)
- VIII. Surfactant are used for extraction of organic pollutant from a contaminated aquifer.

IX. Ammonium hydroxyl propyl trimethyl chloride of guar gum. The most widely used GG derivatives. (Table 2) are hydroxy propyl guar (HPG), carboxy methyl guar (CMG), Carboxy methyl hydroxy propyl guar (CMHPG).

Table 2. Some common derivatives of Guar Gum

Derivative	Structural Substitution	Ionic Charge
Carboxy Methyl Hydroxy Propyl Guar (CMHPG)	CH ₂ -COO-Na ⁺ CH ₂ -CH(OH)CH ₃	Anionic
Carboxy Methyl Guar (CMG)	CH ₂ -COO-Na ⁺	Anionic
Hydroxy Propyl Guar (HPG)	CH ₂ -CH(OH)CH	Non ionic

Figure 4. Guar gum and its derivatives are very important in numerous applications as summarized in.

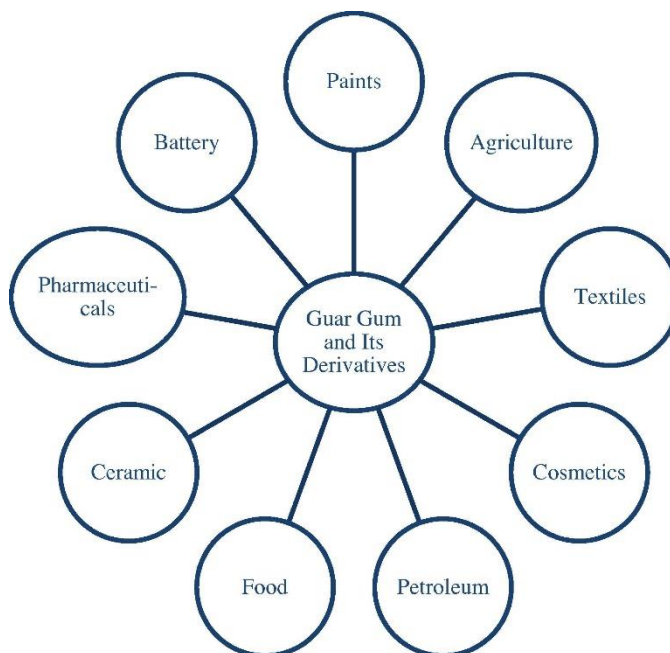


Figure 4. A Various industrial applications of GG and it’s derivative

2. Surfactants

Surfactants are substances that make self-collected atomic groups called micelles in an answer (water or oil stage) and adsorb to the connection point between an answer and an alternate stage (gases/solids). To show these two actual properties, a surfactant should have a substance structure with two distinct useful gatherings with various fondness inside a similar particle.

Typically the atoms of the substances called surfactants have both an alkyl chain with 8-22 carbons. This chain is known as a hydrophobic gathering, which doesn't show proclivity to water. The surfactant particles likewise have a practical gathering called the hydrophilic gathering that has proclivity to water. This sort of construction with two contradicting capacities is called an amphiphilic structure. Surfactants

are characterized into ionic surfactants and nonionic surfactants. Ionic surfactants are sub classified into anionic surfactants where the hydrophilic gathering separates into anions in fluid arrangements, cationic surfactants that separate into cations, and amphoteric surfactants that separate into anions and cations frequently relying upon the pH. Nonionic surfactants will be surfactants that don't separate into particles in fluid arrangements, and they are subclassified relying upon the kind of their hydrophilic gathering (Fig. 5). Normal hydrophilic gatherings of ionic surfactants are carboxylate (- COO⁻), sulfate (-OSO₃⁻), sulfonate (SO₃⁻), carboxybetaine (-NR₂CH₂COO⁻), sulfobetaine (- N(CH₃)₂C₃H₆SO₃⁻), and quaternary ammonium (- R₄N⁺). For instance, a cleanser particle has a hydrocarbon chain as lipophilic utilitarian gathering has partiality to lipids (the lipophilic gathering) and a carboxylate anion as useful gathering has liking to water (the hydrophilic gathering). In a fluid arrangement, the carboxylate anion frames a design with counterions like Na⁺, K⁺, or Mg²⁺. The hydrophilic gathering of nonionic surfactants is typically a polyoxyethylene bunch, yet there are likewise nonionic surfactants with glyceryl gatherings or sorbitol gatherings, and nonionic surfactants with these different hydrophilic gatherings are additionally utilized relying upon the application.

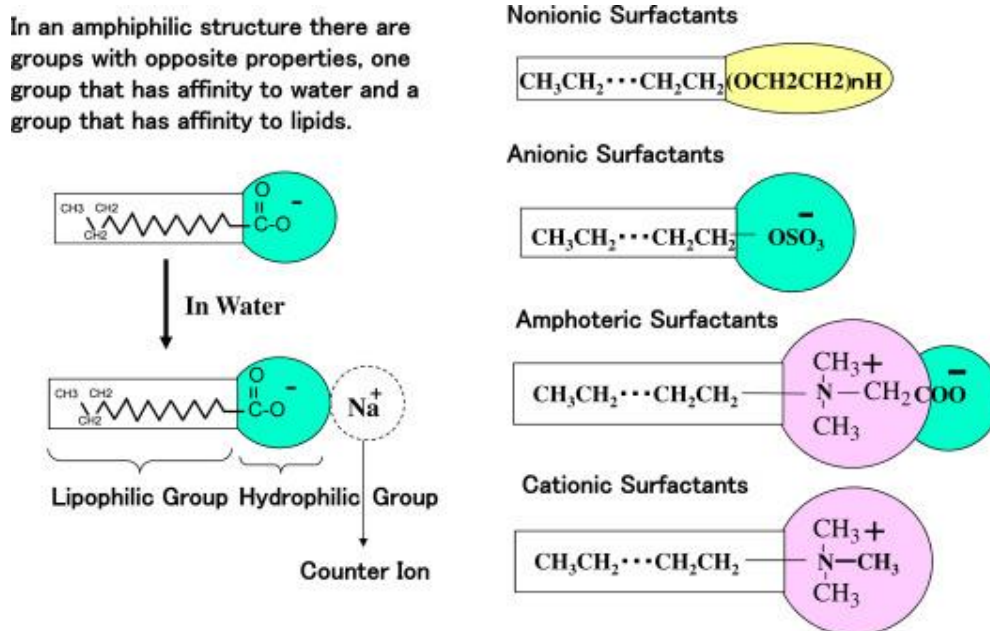


Fig. 5 Hydrophilic Gathering

Surfactants are likewise arranged relying upon their dissolvability, for example, hydrophilic surfactants that are solvent in water or hydrophobic (lipophilic) surfactants that are dissolvable in lipids. Ionic surfactants are by and large hydrophilic surfactants, yet nonionic surfactants can be either hydrophilic or lipophilic, contingent upon the equilibrium between the hydrophilic gathering and lipophilic gathering. At the end of the day, the solvency of nonionic surfactants relies upon the harmony between the hydrophilic gathering's ability of drawing in water and the lipophilic gathering's ability of drawing in oil. Hydrophilic-lipophilic equilibrium (HLB) is a pointer that measures this relative equilibrium. HLB was first proposed by Griffin¹ and at present a few equations to compute HLB have been reported. 2,3 Since HLB shows the attributes of nonionic surfactants, it is usually utilized as a pointer for picking a surfactant for explicit applications, for example, emulsifiers or cleaning agents in Fig. 6. Notwithstanding, since HLB is just a marker in view of involvement, it very well may be utilized as a source of perspective to pick a surfactant for an application however this isn't enough in plan advancement and that can prompt many difficulties. Knowing the attributes of surfactants proficiently and rapidly is essential in plan advancement.

Notwithstanding the HLB, there are two markers that emotionally show these qualities: the cloud point for nonionic surfactants and the Krafft point for ionic surfactants.

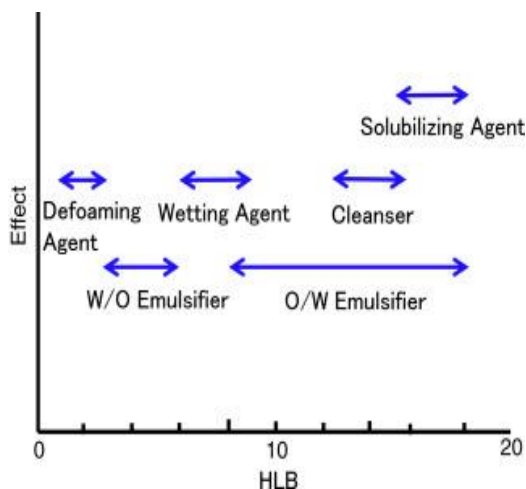


Fig. 6-Emulsifiers or cleaning agents

2.1 Surfactant Types

According to the composition of their head, surfactants are classified as: anionic, cationic, non-ionic and amphoteric.

Anionic surfactants: These surfactants have anionic functional groups like sulphate, phosphate, and carboxylates at their head. Ammonium lauryl sulphate, sodium lauryl sulphate, and similar alkyl-ether sulphates are examples of prominent alkyl sulphates. Sodium lauryl sarcosinate and fluorosurfactants based on carboxylates, such as perfluorononanoate, are examples of more specialised species. For instance, sodium dodecyl sulphate [$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}^+$], sodium dodecyl benzene sulphate [$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$], and sodium stearate.

Cationic Surfactants: Octenidine dihydrochloride is a primary, secondary, or tertiary amine that is pH-dependent; primary and secondary amines become positively charged at pH 10. The quaternary ammonium compounds cetrimonium bromide (CTAB) and benzalkonium chloride (BAC) are permanently charged. For instance, cetyl trimethylammonium bromide [$\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}$] and laurylamine hydrochloride [$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+\text{Cl}^-$],

Zwitterionic surfactants: Zwitterionic (amphoteric) surfactants feature a single molecule that is connected to both a cationic and an anionic centre. Primary, secondary, or tertiary amines and quaternary ammonium cations are the foundation of the cationic component. Sulfonates can be a part of the anionic component, which can be more changeable. The most prevalent biological zwitterionic surfactants, such as phosphatidylserine and sphingomyelin, have the same phosphate anion with an amine and/or ammonium. Dodecyl Betain [$\text{C}_{11}\text{H}_{23}\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}$] for instance.

Non-ionic: These surfactants are oxygen-containing hydrophilic groups that have been covalently joined to hydrophobic parent structures. As a result of hydrogen bonding, oxygen groups are definitely water soluble. The solubility of non-ionic surfactants in water also reduces as temperature rises because hydrogen bonding weakens with temperature. E.g. Alcohol from polyoxyethylen [$\text{C}_n\text{H}_{2n+1}(\text{OCH}_2\text{CH}_2)_m\text{OH}$] Ethoxylate of alkylphenol [$\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_n\text{OH}$] [20].

Composition and structure:

Surfactants are typically natural mixtures that are amphiphilic, meaning they contain both hydrophobic gatherings (their tails) and hydrophilic gatherings (their heads) [21]. Therefore, a surfactant contains both a water-insoluble (or oil-dissolvable) part and a water-solvent part. Surfactants will diffuse in water and

adsorb at interfaces among air and water or at the connection point among oil and water, for the situation where water is blended in with oil. The water-insoluble hydrophobic gathering might reach out of the mass water stage, very high or into the oil stage, while the water-dissolvable head bunch stays in the water stage. World creation of surfactants is assessed at 15 million tons each year, of which about half are cleansers. Different surfactants delivered on an especially enormous scope are straight alkylbenzene sulfonates (1.7 million tons/y), lignin sulfonates (600,000 tons/y), greasy liquor ethoxylates (700,000 tons/y), and alkylphenol ethoxylates (500,000 tons/y).

2.2 Dynamics of surfactants at interfaces:

The elements of surfactant adsorption is vital for pragmatic applications, for example, in frothing, emulsifying or covering processes, where air pockets or drops are quickly created and should be settled. The elements of assimilation rely upon the dispersion coefficient of the surfactant. As the connection point is made, the adsorption is restricted by the dispersion of the surfactant to the connection point. On the off chance that such a hindrance restricts the adsorption rate, the elements are supposed to be 'actively restricted'. Such energy obstructions can be expected to steric or electrostatic aversions. The surface rheology of surfactant layers, including the versatility and consistency of the layer, assume a significant part in the steadiness of froths and emulsions.

2.2.1 Interaction of Guar Gum with Surfactant in Aqueous Medium:

AFM, conductometry, microcalorimetry, and viscometry techniques have all been used to examine the interactions of guar gum (GG) with surfactants like cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), and p-tert-octylphenoxypolyoxyethylene ether (TX-100). Guar gum and CTAB reacted more strongly than DTAB. Results from viscometry help the configurational changes that guar gum molecules go through as they interact with surfactants. AFM measurements were used to establish the geometry of pure GG and their dried states CTAB associated products. Critical aggregation concentration (CAC) is known as the interaction between surfactants and water soluble polymers resulting in the early aggregation of surfactants along with small micelles formation at a concentration lower than critical micelle concentration. Formation of normal micelles by the self-assembling of surfactants in the solution after the completion of interaction between the polymers and the monomers along with small assemblies at a concentration higher than CMC is known as extended CMC or CMCs.

2.2.2 Cationic guar gum and surfactant interactions in diluted and semi-diluted solutions: A type of modified guar gum called cationic guar gum (CGG) has quaternary ammonium groups in place of some of the partial hydroxyl groups. Gum has cationic characteristics when quaternary ammonium groups are added. The use of dynamic and static light scattering to study the interaction of fluorinated cationic guar gum (FCGG)-surfactants with mixed solutions of cetyl trimethyl ammonium bromide [22].

2.2.3 Interactions between CMG and CTAB:

Within the sight of CTAB with varying concentration, the consistency of mixture as an element of shear rate for CMG concentration at 25°C is introduced in Figure 7. Similarly within the sight of CTAB, CMG showed shear rate increment in the shear- diminishing performance. In like manner, for aqueous CMG solution at 25o C in figure-8 explains the zero-shear viscosity as the function of CTAB. It very well may be discovered that with increasing CTAB concentration there is twofold rate increment in the zero- shear viscosity. At low CCTAB, zero-shear viscosity is very small and almost constant at CCTAB/0-1.5 mM [23]. By joining the trial results above, it appears that zero-shear viscosity is higher if the surfactant is more hydrophobic. Be that as it may, the outcomes acquired from CMG within the sight of gemini are at chances with the assumption above, which gave a fascinating wonder [24].

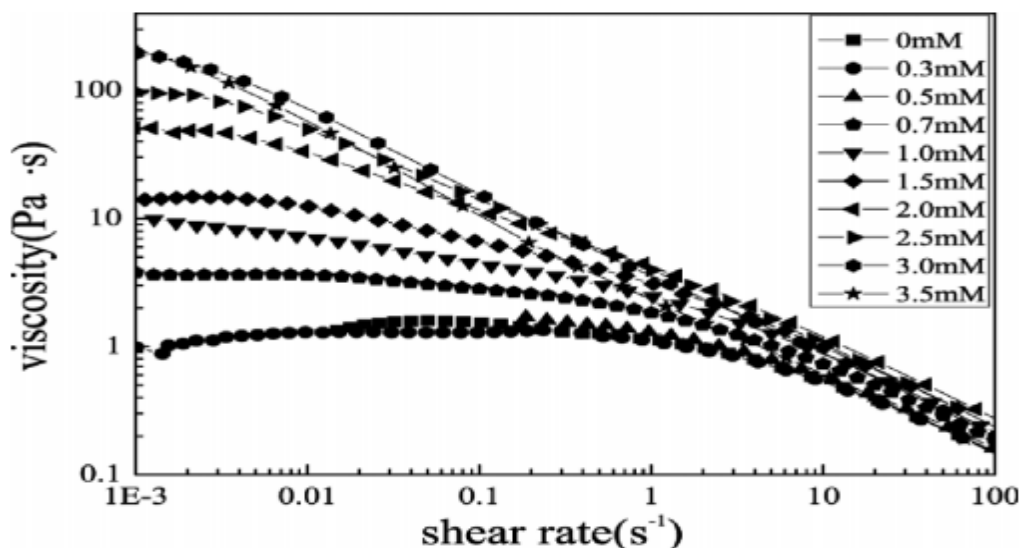


Figure 7. Different shear rate with the various amounts of CTAB of a viscosity of CMG solution (0.6 wt %) at 25°C

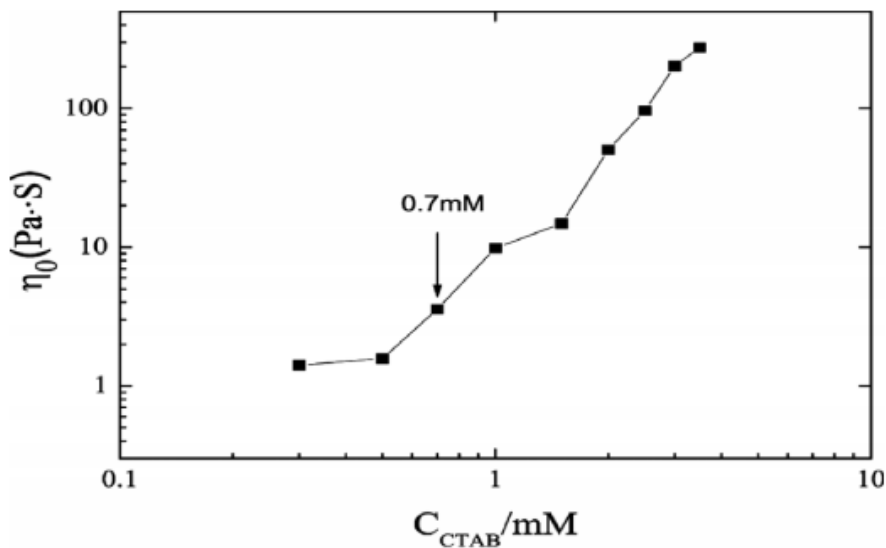


Figure 8: CMG solution (0.6 wt %) with zero shear viscosity as a function of CTAB at 25°C

3. Conclusion

It is very useful and interesting to study and explore guar gum. It's thickening and stabilizing property comes from its hydrogen bond making tendency inside water. Also it has very high viscosity in aqueous solution. All these properties make it a better choice for the applications in the industries like paper, oil, paint, food industries. Also it finds great usage in explosive and cosmetics industry for its low cost. In this study, it is examined how fluorinated cationic guar gum (FCGG) affects ionic surfactant in diluted and semi-diluted solutions, respectively. The topic of discussion was how anionic Carboxy Methyl Guar (CMG) interacted with cationic surfactants including DTAB, TTAB, and CTAB. Because hydrophobic

contact is strengthened by the DTAB in the CMG solution, the amount of polymer-associated aggregates in the TTAB/CMG rises.

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