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HYDROCOLLOIDS AS FOOD EMULSIFIERS AND STABILIZERS

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Abstract

Hydrocolloids are water-soluble biopolymers consisting of high molecular weight polysaccharides known as viscosity builders, gelification agents and stabilizers of food systems.

Several hydrocolloids such as gum arabic (acacia), tragacanth, xanthan and certain modified gums have been mentioned as food additives having special functions such as: "retardation of precipitation of dispersed solid particles and coalescence of oil droplets". The role of these gums as emulsifiers remained somewhat obscure. The present review is an attempt to bring the relevant studies together and to throw some light on the functionalities of the gums as surface active agents and food emulsifiers. In addition, some recent results obtained in our laboratory are discussed.

Gum arabic is compared to colloidal microcrystalline cellulose (MCC) and galactomannans (recent results) in view of their ability to reduce surface tensions, interfacial tensions and to stabilize oil in water emulsions via the 'steric' and 'mechanical' stabilization mechanisms.

It is demonstrated that while gum arabic adsorbs strongly and effectively onto the oil droplets via its proteinaceous moieties, guar gum and locust bean gum (LBG) adsorb weakly and for the most part only "precipitate" on the oil surface, and form birefringent layers of the polymer oriented with its hydrophobic mannose backbone facing the oil. The stabilization with MCC is claimed to be achieved via adsorption of solid particles on the oil droplets (mechanical stabilization).

Key Words: Hydrocolloids, food emulsifiers, food stabilizers, food emulsions, gums, galactomannans, gum arabic.

Introduction

Water soluble high molecular weight polysaccharides have been known for generations as food stabilizers; the main application being modification of the rheological properties of aqueous systems, viscosity builders, gelification agents and stabilizers (Whistler, 1973; Glicksman, 1969; BeMiller, 1988; Dickinson, 1988).

The primary beneficial effect was related to the ability of the hydrocolloid to interact with water and change its rheological properties. However, the functionality of certain hydrocolloids was correlated also to phenomena such as: "retardation of precipitation of dispersed solid particles", "decreased creaming rates of oil droplets and foams", "prevention of aggregation of dispersed particles", "prevention of syneresis of gelled systems containing oils", and "retardation of coalescence of oil droplets" (Dickinson, 1988). Those functionalities are difficult to explain in terms of viscosity and water-gum interactions. Adsorption onto, or interaction with the oil phase had to be considered in oil-in-water emulsions. Adsorption of solid particles had to be adapted for solid dispersions of solid particles in aqueous systems (Tadros and Vincent, 1983).

Most of the water soluble polysaccharides are known to be high molecular weight polymers with a limited number of repeating monomers composing the polymer, low hydrophobicity and limited flexibility (derived from the rotational restrictions of the functional groups), and interfacial density packing limitations. This is contrary to proteins that are composed of both hydrophilic and hydrophobic moieties, which display a high degree of flexibility and hydrophobicity (Figure 1; Yalpani, 1988). It is therefore believed that gums will adsorb (onto solid or liquid surfaces) very slowly, weakly and with very limited surface load if at all (Stainsby, 1988).

Nevertheless, certain polysaccharides, i.e., gum arabic (Banerji, 1952; Silber and Mizrahi, 1975), xanthan (Prud'homme and Long, 1983), and tragacanth (Dea and Madden, 1986; Bergenstahl et al., 1986; Yokoyama et al., 1988) have been noted to display specific surface activities and stabilize dispersed particles of oil droplets in aqueous systems.
Dickinson and Stainsby (1988) distinguish between emulsifiers and stabilizers in food systems and stress the difference between the two using an interesting definition: "An emulsifier is a single chemical or mixture of components having the capacity for promoting emulsion formation and short term stabilization by interfacial action. A stabilizer is a single chemical component or mixture of components which can offer long term stability on an emulsion, possibly by a mechanism involving adsorption but not necessarily so." This definition will be referred to as a guideline for determining efficacy of an emulsifier or stabilizer later in this paper.

In considering stability with respect to coalescence and flocculation, it is important to distinguish between adsorbing polymers and non-adsorbing polymers. Covering particle surfaces with a thick protective layer of adsorbing polymer inhibits coalescence. The coated particles strongly repel one another at close range through a combination of polymeric elastic and osmotic effects, and at this point, the colloid is said to be sterically stabilized. This type of stabilization is most effectively achieved using copolymers having a combination of anchoring groups and dangling chains. The anchoring groups should have a strong affinity for the surface and a low affinity for the continuous phase, and the opposite is true for the dangling chains. In addition, there should be enough adsorbing copolymer to cover the particle surface quite completely, and the layer thickness should be sufficient for two particles to be prevented from approaching a pair separation of which the interparticle (Van der Waals) attraction is of an appreciable magnitude in relation to the thermal energy, kT. A
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high molecular mass favors thick film formation and thus good steric stabilization (Figure 2). A homopolymer composed of many identical adsorbing segments is not a good steric stabilizer, since it produces too thin a layer, leading to free energy interaction with an attractive minimum, whose depth may be several kT (Figure 3).

Where surface coverage is incomplete, a single polymer chain may become attached to more than one particle, as illustrated in Figure 3. Such bridging flocculation is most likely when the polymer concentration is approximately half of that required for saturation coverage (Dickinson, 1988).

As a result, it seems clear that proteins known to have significant hydrophobicity and flexibility, can readily adsorb onto particles or oil droplets, and therefore, will be considered as emulsifiers with short term stability action on dispersed particles (termed "steric stabilization mechanism" by Dickinson and Stainsby, 1988).

Hydrocolloids, on the other hand, will be considered as stabilizers with limited adsorption ability and long term stability (termed "depletion stabilization mechanism" by Dickinson and Stainsby, 1988).

Recent studies have concentrated on the role of gum arabic as an emulsifier, mainly in order to understand the nature of the strong adsorption to the oil droplets in cloudy emulsions for beverages (Randall et al., 1988; Williams et al., 1990).

The present paper is an attempt to critically review the literature with regard to the use of hydrocolloids as food emulsifiers, to analyze their activity at the interface and to evaluate their ability to stabilize emulsions. In addition, some recent results from our laboratory on the use of galactomannans as macromolecular surfactants for possible food applications are presented.

Hydrocolloids as Emulsifiers

The hydrocolloids were classified according to their activity at the interface. Gum arabic is probably the most studied hydrocolloid that proved significant surface activity. Emulsions, as an example of biopolymers and galactomannans, are hydrocolloids with significant rigidity and water-solubility. Micro crystalline cellulose (MCC) is an example of a hydrocolloid with no solubility in water that adsorbs mechanically at the interface.

Gum Arabic

It is well documented that gum arabic, a natural polysaccharide, has excellent emulsification properties for oil-in-water emulsions (Dea and Madden, 1986; Bergenstahl et al., 1986; Yokoyama et al., 1988; Dickinson and Stainsby, 1988; Randall et al., 1988). It is widely used in food, cosmetics and pharmaceutical applications. An excellent example of its use is in cloudy emulsions, as opacity builders for citrus beverages (Williams et al., 1990). Gum arabic is added at high levels (up to 20%) to an aqueous sugar solution and emulsified with an oil phase (Figure 4) consisting of orange oil, and possibly weighting agents (i.e., brominated vegetable oil - BVO, sucrose esters, sucrose diacetate hexaisobutyrate or ester gums). Stable oil-in-water emulsions with high opacity and low creaming are obtained. Gum arabic is known also to form simple coacervates together with other polymeric materials and to encapsulate various oils within the coacervated particles (Glicksman, 1982).

The controlled reaction at pH 8 in the presence of salts between oppositely charged gum arabic and gelatin is a good example of this, yielding coacervate for an application such as soluble coffee (Glicksman, 1982).

Gum arabic (Figure 5), was found to consist of galactopyranose backbone chain linked β-(1-6) to various branches containing arabinofuranose, arabinopyranose, rhamnopyranose, glucuronic acid and 4-O-methyl glucuronic acid (Street and Anderson, 1983; Churms et al., 1983). Gum arabic is always "contaminated" with proteinaceous matter.

The role of the proteinaceous components in gum arabic was subject to several recent studies. Anderson (1986) reported that the small amount of proteinaceous material is an integral part of the gum structure. Vandevelde and Fenyo (1985) and Connolly et al. (1988) related the significance of this fraction to the molecular

![Figure 4. The average droplet diameter of emulsions (20% w/w orange oil) as a function of gum arabic concentration. Measurements were performed on diluted dispersions (1/1000) with distilled water using a ZM model Coulter counter equipped with a 50 μm orifice electrode.](image-url)
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D-GlcpA
1
\( \rightarrow 3 \)

6
R\( \rightarrow 3 \)-D-Galp
1
\( \rightarrow 3 \)

6

\( \rightarrow 3 \)-D-Galp(1\( \rightarrow 3 \))-D-Galp(1\( \rightarrow 3 \))-D-Galp(1\( \rightarrow 3 \))-D-Galp(1\( \rightarrow 3 \))-D-Galp(1\( \rightarrow 3 \))-D-Galp(1\( \rightarrow 3 \))-D-Galp

D-GlcpA = D-glucopyranosiduronic acid
D-Galp = D-galactopyranose
L-Rhap = L-rhamnopyranose
L-Arap = L-arabinopyranose
L-Araf = L-arabinofuranose
R = 1.-Rhap (1\( \rightarrow 1 \)), 1.-Araf (1\( \rightarrow 1 \)), D-Galp (1\( \rightarrow 3 \))-1.-Araf (1\( \rightarrow 1 \)), or 1-Arap (1\( \rightarrow 3 \))-1.-Araf (1\( \rightarrow 1 \)).

Figure 5. Schematic structure of the polysaccharide portion of gum arabic.

Figure 6. Emulsification capability of heat pre-treated gum arabic solutions as monitored by the average droplet size diameter in orange oil (20% w/w) emulsions using gum arabic (19% w/w) heated for various times at 100°C. characteristics and properties of the gum. They showed that the gum consisted of two distinct fractions namely a high molecular mass arabinogalacto-protein complex (AGP; representing about 30% of the total) and a lower molecular mass fraction.

It was demonstrated that the emulsification capability of heat treated gum arabic was reduced dramatically due to the denaturation effect of the "active" protein (Figures 4 and 6). A similar effect was recorded at a low pH. In a more recent work, Randall et al. (1989) showed that the gum consisted of three distinct fractions: a high molecular mass arabinogalacto-protein complex (AGP) glycoprotein (G1), and lower molecular mass fraction which was protein deficient (AG). The AGP fraction was shown to be degraded by proteolytic enzymes with the molecular mass decreasing to a value similar to that of the AG fraction (Randall et al., 1989). It was suggested that the AGP fraction consists of about five carbohydrate blocks of molecular mass 2.8 \times 10^5 linked together by a polypeptide chain, which may contain as many as 1600 amino acid residues. It is likely that the polypeptide chain is located at the periphery of the molecule, thus facilitating its adsorption onto hydrophobic substances. The AG fraction is not degraded by proteolytic enzyme and may simply be a fragment of AGP fraction. At relatively low concentrations, gum arabic yields solutions, which are essentially Newtonian in behavior and have very low viscosities compared to other polysaccharides of similar molecular mass. This behavior is similar to globular proteins. The intrinsic viscosities of gum arabic are similar to those of \( \beta \)-lactoglobulin. The intrinsic viscosities of gum arabic solutions reach their maximum at pH 5-5.5. Randall et al. (1988) and Williams et al. (1990) have recently reviewed the structure of the various fractions in gum arabic and concluded that the high molecular mass AGP fraction is responsible for the gum’s emulsifying ability. The complex structure of AGP, where hydrophilic carbohydrate blocks are linked to the main polypeptide chain, enables strong adsorption at O/W interfaces. Only a small amount of the gum (high molecular weight) does actually adsorb onto the oil droplets (good correlation in permeation chromatogram of a solution of gum arabic monitored before and after preparing an orange oil emulsion). Consequently, relatively high concentrations of gum arabic are required to produce stable emulsions of relatively small droplet size. At a lower gum arabic concentration, there is insufficient surface active material to fully coat all the droplets. Randall et al. (1988) and Williams et al. (1990) have also demonstrated that the two glycoprotein components of the gum (AGP and G1) are denatured on heating, resulting in a loss of emulsification capability and a reduction in solution viscosity.
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Table 1. Surface pressure $\pi$ and surface viscosity $\eta$ of adsorbed films of gum arabic after 24 hours at the n-hexadecane-water interface (0.005 M, 25°C).

<table>
<thead>
<tr>
<th>pH</th>
<th>$\pi$/mN m$^{-1}$</th>
<th>$\eta$/mN m$^{-1}$s</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>1.0$^3$</td>
<td>7.0$^3$</td>
</tr>
<tr>
<td>2.3</td>
<td>1.0$^2$</td>
<td>7.0$^2$</td>
</tr>
<tr>
<td>7.0</td>
<td>1.0$^3$</td>
<td>7.0$^3$</td>
</tr>
</tbody>
</table>

(I) A. criopoda (5.27% N)  19 16 220 200

(II) Commercial sample (0 36% N)  4 4 11 10 1

(III) A. ampliceps (0 10% N)  9 < 1 < 1

Dickinson et al. (1988a,b, 1990) noted the dependence of the nitrogen content (in several Acacia and Arabic gums, in the range of 0.1-5.27 wt%), on the time-dependent droplet size distribution of n-hexadecane-in-water emulsions (Table 1). It can be seen that Acacia gum with the highest nitrogen content (5.27% N) resulted in emulsions with the highest surface pressure ($\pi$) and surface viscosities ($\eta$) at any of the pH levels (Dickinson, 1988). Dickinson et al. (1991) also showed that the molecular weight of gum arabic had an effect on its emulsifying behavior and concluded that the protein-rich, high molecular-weight component (the arabinogalacto-protein complex) is the fraction that provides the functionality of the gum arabic as an emulsion stabilizer.

Therefore, the best emulsion capacity and emulsion stability (in regard to both coalescence and flocculation) was recorded in gums with highest nitrogen content. Those emulsions exhibited high surface viscosity as well, which did not change upon dilution (Dickinson et al., 1989). Stable and deflocculated emulsions should be covered with adsorbed polymer that fulfills the following criteria: full coverage, firm anchoring, thick layer and low redesorption.

It seems that the protein-hybrid in gum arabic meets all the necessary requirements in a capacity similar to emulsifying proteins (such as casein, bovine serum albumin, or soy protein) via its numerous adsorption sites, flexibility, conformational change at the interface and the entropy gain (solvent depletion). Therefore, it has been concluded that although gum arabic is basically a hydrocolloid, its interfacial and emulsifying properties are derived from its proteinaceous nature (Randall et al., 1988).

Schematic illustration of the structure of the arabinogalacto-protein complex at the oil-water interface is shown in Figure 7.

**Figure 7.** Schematic illustration of the arabinogalacto-protein complex structure at the oil-water interface.

**Figure 8.** Effect of protein content on the specific emulsifying activity of different Emulsan preparations.

Other Hydrocolloids

Most hydrocolloids were considered to have poor surface properties and therefore chemical modifications were proposed to improve their activity. Examples of such hydrocolloids are highly substituted methyl cellulose, acetylated pectin, etc. (Dickinson and Stainsby, 1988). The chemically modified gums are beyond the scope of this paper.

However, some natural biopolymers (also known as extracellular natural polysaccharides) exhibit good surface properties. The best example is "Emulsan", consisting of a large proportion of hydrophobic side-chain attached to a sugar backbone. This anionic biopolymer
has excellent emulsifying properties due to the presence of fatty acids linked to the amino-sugar backbone, giving it its amphiphilic character. It combines the hydrophobicity of a protein with the hydrophilicity of polysaccharides (Zosim et al., 1987) (Figure 8).

An additional class of hydrocolloids includes those compounds known to have limited surface activity even though the crude products are contaminated with proteinaceous material. In this category, we could include materials such as xanthan, tragacanth and galactomannans. Some of these polysaccharides have been claimed to have surface activity and promote formation of stable emulsions (Dickinson, 1988).

The main questions to be answered were: (1) What is the role of the proteinaceous matter? (2) How surface active are these in comparison to gum arabic? (3) Do they really adsorb onto the surface of solid or liquid particles? and (4) To what extent does the viscosity (or the depletion action) play a role in the stabilizing properties? In other words, are these materials stabilizers or emulsifiers?

Very little systematic work has been carried out in attempt to solve these questions. The information available in literature is limited at best.

**Colloidal microcrystalline cellulose (MCC)**

Effective stabilization against coalescence of emulsified oil globules can be obtained by using certain finely divided powders as emulsifiers (McGinley et al., 1984; Oza and Frank, 1989; McGinley and Tuason, 1990). Cellulose, in the chemical sense, is a polysaccharide of sufficient chain length to be insoluble in water or dilute acids. It consists of anhydroglucose units linked together through the 1 and 4 carbon atoms with a beta-glucosidic linkage. Fibrous cellulose is composed of millions of microfibrils. The individual microfibril is composed of two regions, the paracrystalline region, which is an amorphous and flexible mass of cellulose chains, and the crystalline region, which is composed of tight bundles of cellulose chains in a rigid linear arrangement (McGinley and Tuason, 1990). Microcrystalline cellulose is a purified, naturally occurring cellulose, produced by converting fibrous cellulose to crystalline cellulose or a dispersible gel.

Microcrystalline cellulose forms a colloidal dispersion of solid particles in water if properly sheared. The cellulose crystals are claimed to set-up a network with the majority of the particles being less than 0.2 μm. Only at this size range can the insoluble cellulose structural network provide the colloidal MCC grades with their functional properties. The strong affinity of cellulose for both the oil and the water results in precipitation and some orientation of the solid particles at the oil-water interface (McGinley et al., 1984). Several methods have been used to detect and evaluate the structures formed on the interface. A mechanical stabilization mechanism was proposed since the solid colloidal particles, precipitate on the interface and prevent collisions by acting as a physical barrier (McGinley et al., 1984). In addition, it was proposed that the colloidal network of
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Figure 10. Rheological properties MCC-guar and oil.

The free MCC thickens the water phase between the oil globules preventing their close approach and subsequent coalescence. Therefore, the MCC provides long term stability (McGinley and Tuason, 1990).

The inherent properties of colloidal MCC products dispersed in water have been used to simulate fat induced rheology in various food applications including ice-cream, salad dressings, sauces, and gravies. The consistency of oil-in-water emulsions can vary from a thin fluid material at low oil levels to a thick viscous paste at very high oil levels. Studies have shown that there is a change in the rheological properties of the emulsions from simple Newtonian behavior to non-Newtonian behavior above an oil concentration of 50 wt% (McGinley and Tuason, 1990).

By incorporating colloidal MCC into the system, the level of oil in the emulsion can be effectively reduced while still retaining their lubrication and flavor carrying properties, as well as rheological properties (McGinley and Tuason, 1990). It has been demonstrated that basic emulsions containing 30% soy oil have similar rheological properties and stability characteristic as 20% soy bean oil emulsions containing 1% colloidal RC-591 or 1.5% CL-611 (Figure 9). [RC-591 and CL-611 are two types of commercial MCC as described in McGinley and Tuason (1990)].

The properties of the soy bean oil are in fact improved using lower levels of oil in conjunction with MCC. The emulsions acquire a yield value which makes the system stable against creaming. It is clear therefore, that microcrystalline cellulose has considerable potential for use as a fat substitute in the formulation of aqueous-based dietary food formulation.

It was also shown that in the wet state, guar gum physically interacts with colloidal crystalline cellulose resulting in the flocculation of the cellulose. Further drying of the "hydrocolloid alloy" (particles made from MCC and guar gum) results in powdered particles that are spherical, shear resistant and water-insoluble (Figure 10) (McGinley and Tuason, 1990).

The insoluble, spherical MCC/guar gum particulates can be agglomerated with a water-soluble hydrocolloid and subsequently dried to readily recover water-dispersable spheroidal particles capable of forming a stable aqueous gel. A potential use for this dried, reconstitutable, spherical form of colloidal microcrystalline cellulose product is in the area of non-nutritive fat substitute for aqueous food systems. The non-nutritive aspects and water-insoluble form of colloidal MCC are key to the development of a successful product for this kind of use. A patent pertaining to a composition and production method for a dried, spherical form of a colloidal microcrystalline cellulose as a non-nutritive and/or low calorie fat substitute in aqueous food systems has been issued (Durand et al., 1970).

Galactomannans

Galactomannans are the most common plant food reserve polysaccharides belonging to the legume family consisting of β-(1-4)-linked D-mannan backbone, stabilized in water, by substitution of: α-(1-6)-linked D-galactose stubs for certain of the mannose residues (Figure 11) (Seaman, 1980).

Great diversity in the chemical structure of the galactomannans derived from different plant sources, was detected (Winter et al., 1984). This diversity includes wide variation in the degree of galactose substitution (galactose/mannose ratio of 1:5) and significant differences in the distribution of galactose substituents along the mannose chain (Winter et al., 1984).

Galactomannans exist as fluctuating random coil chains with non-specific viscosity behavior in aqueous solutions (Winter et al., 1984).
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Figure 12. Schematic illustration of an oil droplet emulsified with lecithin and polysaccharide (polysaccharide serving as viscosity builder).

The main characteristics of galactomannans are related to their thickening properties, self-gelling properties and contribution to gel formation of other hydrocolloids. Differences in structure significantly affect those functionalities. Much has been reported on the structural aspects of the gums, their rheological and interactional behavior in aqueous systems, and their contribution to the emulsification of oil droplets in the presence of monomeric emulsifiers (Figure 12), but very little has been done with respect to their interfacial characteristics.

Galactomannans, as well as other biopolymers, have been evaluated as flocculants in aqueous systems. From preliminary work (Bergenstahl et al., 1986; Lips et al., 1991) on competitive flocculation efficiency on latex particles, it was concluded that guar (and similarly also xanthan gum) adsorption is weak and increases with concentration without going through a maximum (minimum flocculation) in comparison to gelatin, casein or gum arabic that adsorb very strongly and exhibit a clear maximum at low protein concentration (Figure 13).

However, latex surfaces are quite different as compared to oil/water interface in true food emulsions. The ability of a number of industrial gums to act as steric stabilizers of oil/water emulsions, in the presence of different low molecular weight emulsifiers, has been studied (Bergenstahl, 1988). It was found that several gums show a pronounced effect on stability already at the ppm level of concentration. To explain these results, Bergenstahl (1988) proposes that the gums adsorb onto the surfactant layer, forming a combined structure of a primary surfactant layer covered by an adsorbed polymer layer.

Table 2. Interfacial tension of oil/water as measured with and without the addition of LBG (25°C, 720 min.).

<table>
<thead>
<tr>
<th></th>
<th>weight %</th>
<th>η (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetradecane</td>
<td>0</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>25</td>
</tr>
<tr>
<td>Paraffinic oil</td>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>22</td>
</tr>
<tr>
<td>Toluene</td>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>17</td>
</tr>
<tr>
<td>Castor oil</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>12</td>
</tr>
<tr>
<td>Soya oil</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 3. Composition of guar gums at different grades of purification.

<table>
<thead>
<tr>
<th></th>
<th>Commercial (native)</th>
<th>Purified</th>
<th>Bi-purified</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>8.49</td>
<td>12.7</td>
<td>13.1</td>
</tr>
<tr>
<td>Galactomannan</td>
<td>92.2</td>
<td>98.6</td>
<td>99.0</td>
</tr>
<tr>
<td>Ash</td>
<td>0.71</td>
<td>0.25</td>
<td>0.22</td>
</tr>
<tr>
<td>Protein</td>
<td>5.95</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Fiber</td>
<td>1.55</td>
<td>0.19</td>
<td>trace</td>
</tr>
<tr>
<td>Cellulose</td>
<td>1.02</td>
<td>0.19</td>
<td>trace</td>
</tr>
<tr>
<td>Fat</td>
<td>0.92</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>Man./Gal.</td>
<td>3.91</td>
<td>4.58</td>
<td>7.70</td>
</tr>
</tbody>
</table>

Young and Torres (1989) studied the surface properties of xanthan gum by drop weight and Wilhelmy plate methods, and found that the surface tension properties of aqueous xanthan solutions are affected by its molecular conformation in the solution. Xanthan in the random coil conformation was more surface-active than xanthan in the helix conformation. Surface tension decreased and adsorption rate increased significantly by increasing xanthan concentration and by adding 0.1 N NaCl. Surface excess values, calculated by the Gibbs equation, suggested that surface tension was affected by the proportion of molecular segments adsorbed at the interface.

LBG and guar have been recently studied in our laboratory in view of their surface and interfacial properties (Reichman and Garti, 1991). Emulsification capabilities and stability of oil-in-water emulsions have been determined and examined in order to answer the question of the adsorption to the oil interfaces (Reichman and Garti, 1990; Reichman, 1992).
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Figure 13. Comparative flocculation efficiency of food biopolymers (latex diameter 88 nm, particle density $4.5 \times 10^{11}$ cm$^{-3}$, sodium chloride concentration $6.7 \times 10^{-2}$ mol dm$^{-3}$, 28°C, pH 5.9). Δ: dextran 7500; ○: gelatin; □: caseinate; ♦: gum arabic; ●: xanthan; ■: guar (Lips et al., 1991).

Figure 14. Surface tension of aqueous solutions of commercial (native) guar gum and LBG. Δ - for LBG and ■ - for guar gum.

Wilhelmy plate determinations showed that both LBG and guar gum reduce surface tension of water at low concentrations (up to 0.5 wt%) and that the surface tension of the gum solutions is time dependent. The gums are sluggish and slow in their migration to the interface. Equilibrium surface tensions decrease and adsorption rates increase significantly, as expected, by increasing the gum concentration. The lowest surface tensions measured for LBG and guar gum (Reichman and Garti, 1990) were 50 and 55 dynes/cm respectively (Figure 14) in comparison to 42.3 and 43.0 dynes/cm for xanthan and tragacanth gums. The gums do not exhibit clear critical micellar concentration (CMC) at concentrations up to 0.7 wt%. This surface activity seems to be relatively pronounced in view of the chemical structure and expected hydrophilicity.

Interfacial tensions (Table 2) were significantly lower in comparison to other hydrocolloids or well known emulsifying proteins.

It was demonstrated (Reichman, 1992) that at least most of the proteinaceous components are not integral component of the polysaccharide and can be almost entirely removed by repeated crystallization (Table 3). The level of protein contaminating the guar was reduced from 5.95 wt% in the crude commercial guar to 0.8 wt% in our bipurified fraction. However, it should be noted that by our techniques, we could not further remove the protein from the guar and some of the gum can still be "bound" to the protein.

Several guar (or LBG) fractions containing increasing levels of protein have been isolated. The fraction with the lower nitrogen content (bipurified, BP, 0.8% protein) had the best surface properties among all fractions and the fraction with the highest nitrogen levels (precipitate, PR, 10.6 wt% protein) showed the lowest
surface activity. The native guar (5.95 wt% protein) had excellent surface behavior almost similar to the bipurified fraction. Figure 15 shows the interfacial tensions of LBG and guar gum upon concentration.

Relatively large oil droplets (10-60 μm) have been formed when gum solution was emulsified with 5 wt% vegetable oil or tetradecane in the presence of 0.5 wt% gum (Figure 16; Reichman, 1992).

Pretreatment of the gum solution, prior to its use, by heat (8 hours at 90°C) or change in pH (pH 3, 7, 10) did not damage the gum’s capabilities to stabilize the emulsion. This indicates that either the proteinaceous portion of the gum has practically no surface activity or that it was not affected by the drastic pretreatment conditions. We tend to believe that the residual protein does not significantly contribute to the polysaccharide adsorption on the interface (Figure 17).
These two findings after heat pretreatments, along with emulsification still showed the fastest coalescence rates.

The proteimaceous contaminant in the emulsifiers activity at different pH levels, indicate that the gum is not responsible for its surface activity.

Increasing the gum concentration and lowering the oil content facilitated formation of stable emulsions with low coalescence rates. Full coverage of the oil phase was obtained at hydrocolloid to oil ratios \( r = (\text{wt}\% \) hydrocolloid / wt\% oil \( ) \times 100 \) of 18 and up, leading to stable and non-flocculated emulsions (Figure 19).

The adsorption capability of the gum was limited only to certain oils and in many cases strong flocculation and creaming were detected.

Surprisingly, a birefringency effect was observed on emulsion droplets prepared from the gum solutions. The birefringency was affected by the oil concentration, gum levels, method of preparation, dilution, and electrolytes (Figure 20).

The birefringency was attributed to the formation of a thick, well-oriented gum film on the oil droplet. The strong birefringency around the oil droplets can be interpreted also as a formation of a "gum precipitate around the droplets" and/or formation of oriented gel phase around the droplets (see Discussion with Reviewers).

The film formed as a result of a "salting-out" effect on the gum (caused by the addition of oil to the gum solution) which "precipitated" the gum on the oil interface.

Hydrophobic oils show stronger birefringency than more hyrophilic oils. Upon strong dilution \( (x \ 600\text{-}1000) \) the gum quickly desorbs from the surface and loss of birefringency is noted.

The photomicrographs under polarized light (Figure 20) of the oil/water emulsions stabilized by galactomannans, seem to indicate large surface loads (very strong birefringency, mainly on soya oil interfaces) but unfortunately to the best of our knowledge, no quantification method is yet available to correlate the birefringency and the surface concentrations of the polymeric emulsifier.

Therefore, the surface load was evaluated from adsorption isotherms (Reichman and Garti, 1991; Reichman, 1992).

Lower surface loads and surface concentrations are characteristic of the galactomannans in comparison to gum arabic or proteins but are, nevertheless not negligible (Figure 21).

Figure 21 illustrates the isotherms in the adsorption of guar gum and LBG onto the oil-water interface. The surface load is a maximum 4 mg/m\(^2\) for LBG with a total gum concentration of 0.9 g/100 ml and 2.8 mg/m\(^2\) of guar gum. These surface concentrations are lower than those measured for commercial and nitrogen enriched gum arabic (4 and 7 mg/m\(^2\) at 300 mg/dm\(^3\) equilibrium polymer concentration, respectively) as measured for latex adsorption (Dickinson et al., 1989). It should be noted that this adsorption is weak and quite reversible.

Dilution of the emulsions with water will cause fast gum desorption from the interface.
Figure 20. Polarized light photomicrographs of oil/water emulsions stabilized by galactomannans: (A) 0.9 wt% LBG, 5 wt% n-tetradecane; (B) 0.9 wt% guar, 5 wt% toluene; (C) 0.9 wt% guar, 5 wt% soya oil. Photo width (for each micrograph) = 50 μm.

Figure 21. Surface load of guar gum (■) and LBG (▲) in 5 wt% tetradecane in water emulsions prepared with 0.1 to 0.9 gr/dl gum in the aqueous phase.
Hydrocolloids as Food Emulsifiers and Stabilizers

Conclusions

It was demonstrated that guar and gum arabic stabilize oil-in-water emulsions. However, it seems that the two types of gums behave in different modes at oil-water interfaces. The gum arabic behaves as a typical surface active protein and anchors strongly to the oil phase via its proteinaceous part of the molecule. When the proteinaceous part is removed, denatured, or deactivated, the gum tends to lose its surface activity and emulsification capability. Only a small part of the gum mixture is responsible for its activity and therefore, large excesses of gum are required to obtain stability.

It appears that the spheroidal shape of the gum arabic together with the proteinaceous portion attached to the polysaccharides facilitate alignment and close-packing of the gum at the oil-water interface. Spatial separation of the relatively hydrophobic portions of the gum molecule, (i.e., methyl groups of rhamnose in the terminal position) from the hydrophilic hydroxyl and ionic regions appears to have a significant effect on its surface activity (Randall et al., 1988; Anderson, 1978). Perhaps the minor polyphenolic component of the gum is also effective in the same sense, though there are indications that other hydrophobic associations may also be responsible (Ettling and Adams, 1968).

Gum tragacanth (not discussed in detail in this review) is an effective emulsifier at as low a concentration as 0.25 wt%, with significant hydrophobicity being attributed to the terminal deoxyhexosyl groups of tragacanthic acid, while the spheroidal arabinono-galactan component acts like the polysaccharide component of gum arabic (Stephen, 1990).

On the other hand, galactomannans, being very hydrophilic polymers with rigid structures, migrate to the oil interface slowly and only after applying high shears. The oil helps to "precipitate" the hydrophobic portions of the polymer that tend to adsorb on the oil. It adsorbs very weakly, but forms ordered and oriented thick films (possibly gelled films) that reveal high birefringency. The emulsification ability is weak and high gum to oil ratios are required to retard coalescence and reduce flocculation of the oil droplets.

The addition of small molecule surfactants, dilution, along with heat application, etc. will desorb the gum from the interface and will speed coalescence and rupture of the emulsion (Garti and Reichman, 1994).

Much work is required in order to better illustrate the ability of galactomannans to adsorb the oil droplets and to stabilize the oil/water emulsion via a steric stabilization mechanism. It will be even more difficult to explain the nature of this adsorption. Is the polysaccharide adsorbed in a molecular form or as a solid colloidal particle, much like MCC?

At present, enzymatic treatment of the guar gum is being done in our laboratory in order to achieve an efficient "degalactosidation" of the mannose backbone and to clarify the role of the backbone and the side chain groups in the emulsification behavior of the gum. Competitive adsorption with proteins, small molecule surfactants, and other hydrocolloids is also being carried out.

Extensive work is being done at present in order to better characterize the oil-water interface in the presence of the hydrocolloid using more advanced methods such as cryo-scanning electron microscopy, small angle X-ray scattering (SAXS), and small angle neutron scattering (SANS).

Colloidal microcrystalline cellulose stabilizes oil-in-water emulsions by a mode known as "mechanical stabilization" of solid powdered colloidal particles precipitating on the oil droplets.

References


N. Garti and D. Reichman


Hydrocolloids as Food Emulsifiers and Stabilizers


Discussion with Reviewers

H.A.C.M. Hendrickx: Can the authors explain why the denaturation of the protein in gum arabic fractions AGP and G1 leads to a reduction in solution viscosity?

Authors: Williams et al. (1990) studied the structure-function relationship of gum arabic and have shown that gum arabic can be separated into three principal fractions: an arabino-galactan (AG); an arabinogalacto-protein complex (AGP); and glycoprotein (G1). Gum arabic solutions at low concentrations are essentially Newtonian in behavior and have very low viscosities compared to other polysaccharides of similar molecular mass. No data on the differences in the viscosities of AGP and AG (or 31) are available, but we can assume that since AG appears to be the hydrocolloid (polysaccharide) fraction of the AGP, its viscosity will be much higher (similar to guar gum or LBG) than the viscosity of AGP. Gum arabic has been shown to be heat sensitive and some precipitation will occur on prolonged heating. The precipitate has been shown to be essentially the proteinaceous material and the gel permeation chromatography indicates that both AGP and G1 fractions are removed. As a consequence of the loss of the high molecular mass AGP fraction, the solution viscosities decrease considerably. Williams et al. (1990) explain that the reduction in the gum viscosity is due to the removal of the AGP and G1 fractions from the solution. They do not correlate the viscosity reduction to the denaturation of the AGP or G1 fractions. It is difficult, in our opinion, to see why the polysaccharide fraction AG, that is left in the solution, will have lower viscosities than the protein-polysaccharide complex, but it is an experimental fact (Williams et al., 1990). The giant difference in the MW of the two fractions may be the reason for this. Figure 7 is a schematic illustration of the adsorption of AGP fraction of the oil-water interface. The sketch was drawn by Randall et al. (1989) to illustrate the role of the protein in the arabino-galacto-protein complex. We agree with the comment that probably most of the protein adsorbs on the oil/water interface with its hydrophobic side groups in the oil phase and the hydrophilic groups facing the water, and the polysaccharide is most probably mostly in the water. However, those are pure speculations, without any good evidence. The authors’ intention in this schematic illustration was to demonstrate that the protein, rather than the polysaccharides, adsorb on the interface.

E. Dickinson: The substantial reduction in emulsifying capacity caused by pre-heating of gum arabic is attributed to “denaturation” of the glycoproteinic components of the hydrocolloid. This is certainly a possibility, although I am sure you will be aware that heat-induced unfolding of globular proteins can often lead to improved emulsifying properties so long as there is no protein coagulation. For gum arabic, is there any evidence of loss of solubility of change in molecular weight on heating? We have found that a sample of gum arabic that had been partially degraded by irradiation gave poorer emulsion stability than the native gum; this was attributed by us to poorer steric stabilization caused by the lower average molecular weight of the gum as indicated by intrinsic viscometry. In principle, extended heating of gum arabic could lead to slow degradation of the hydrocolloid into smaller fragments, although I suspect that aggregation arising as a result of protein denaturation and coagulation is probably more likely, especially in the early stages of the heat treatment.

Authors: Pre-heated gum arabic solutions showed lower emulsification capability in comparison to untreated solutions. The authors (Dickinson, 1988; Randall et al., 1989) attributed it to the denaturation phenomena. We are aware that heat-induced unfolding of globular proteins can lead to improved emulsifying properties. We do not know at present what was the heat treatment effect on the proteinaceous fraction contaminating the galactomannans. All we claim is that the heat treatment did not damage the gum capabilities (unlike the effect it had on gum arabic). Close reexamination of our results can indicate even high improvement in the droplet size distribution at time zero and after one week. However, the pH change did not reflect in its activity.
E. Dickinson: You seem to be suggesting that the surface activity of guar gum and locust bean gum is greater at the oil-water interface than at the air-water interface. If Figure 14 refers to equilibrium (steady-state) tensions, then the speed of migration to the interface is irrelevant. I am skeptical as to whether really pure xanthan is as surface-active at the air-water interface as you indicate; many commercial samples of xanthan contain cell wall fragments, which can be proteinaceous and hence surface-active. You also say that tensions for locust bean gum at oil-water interfaces are lower than for well-known emulsifying proteins. If you are referring here to milk proteins, I find this difficult to accept.

Authors: Figure 14 refers to equilibrium surface tensions of guar gum and LBG. We are aware that "xanthan contains cell wall fragments and can be proteinaceous and hence surface-active"; the xanthan gum results are not from our experimental work. We used guar that was twice purified. LBG reduces interfacial tensions quite remarkably. However, we admit that some food including milk proteins are more efficient than LBG in reducing interfacial tensions.

E. Dickinson: Why does heat treatment of guar gum lead to smaller emulsion droplets than with native hydrocolloid (Figure 17)?

Authors: We do not have a good explanation for these findings. We repeated the experiments several times and the results were reproducible. Possible explanations are related to: (1) the role of the protein fraction in the gum, or (2) possible gum reorganization in the solution leading to some orientation in the random coils.

E. Dickinson: The birefringence of the adsorbed guar gum layer is said to be lost on dilution. Is the emulsion, therefore, destabilized on dilution?

Authors: Yes, the emulsion loses both the birefringency and its stability upon dilution. We attribute it to a gum desorption from the oil interface. The gum is weakly adsorbed/precipitated and dilution causes "salting in" effect and redisolution of the gum in the water.

L.K. Jackson: What evidence do you have that gum arabic is spherical?

Authors: We do not have any direct evidence for such claim. However, Randall et al. (1988, 1989) studied its rheological properties and concluded that its viscosity in water at low concentrations is similar to β-lactoglobulin, which is a globular protein. There are more similarities of the gum arabic behaviour that resemble the globular proteins.

B. Bergenstahl: Figure 20 shows emulsions with 5% dispersed phase. However, it appears that the number of droplets is very small (when compared to the concentration) in Figures 20A and 20B. Please comment.

Authors: The concentration of the emulsion in Figure 20 is indeed 5% dispersed phase. We believe that the photograph was taken from an area "on the slide" that was diluted for convenience reasons.

B. Bergenstahl: An adsorbed polymer layer is usually not observed as a birefringent layer around the droplets. The observation in Figure 20 has to be interpreted as a precipitated and/or oriented gel phase around the droplets. If we assume that the birefringent layer is an oriented gel phase, a similar birefringent layer should be observed around the air-water interface on the edge of the microscopic slide. Was this observed?

Authors: We repeated the experiment as per your suggestions. We did not see birefringency around the air-water interface on the edge of the microscopic slide. However, we are not ruling out the interpretations suggesting that the gum forms a precipitated and/or oriented gel phase around the droplets. As a matter of fact, we believe that this might indeed be the case. We assume that the birefringency is seen only when "salting-out" conditions are dominating the system (i.e., in the presence of oil droplets).

B. Bergenstahl: The emulsions produced in the experiments are usually fairly coarse, with average sizes around 10 μm. In emulsions with large droplets, the Brownian flocculation will be very slow and gravity induced flocculation (Reddy, Melik and Fogler, J. Colloid Interface Sci. 82, 116-27, 1981) will be the main flocculation mechanism. Would it be possible that the stabilization of the emulsion is due mainly to the formation of a loose gel [Walstra in "Food Emulsions", Dickinson (ed.), 1986, p. 242-59]? What type of effects were observed on the rate of creaming?

Authors: The possibility that the stabilization of the emulsion may be induced by the formation of loose gel was considered. Most emulsions are free-flowing and non-viscous. Therefore, since guar gum does not form gels, we excluded this possibility.