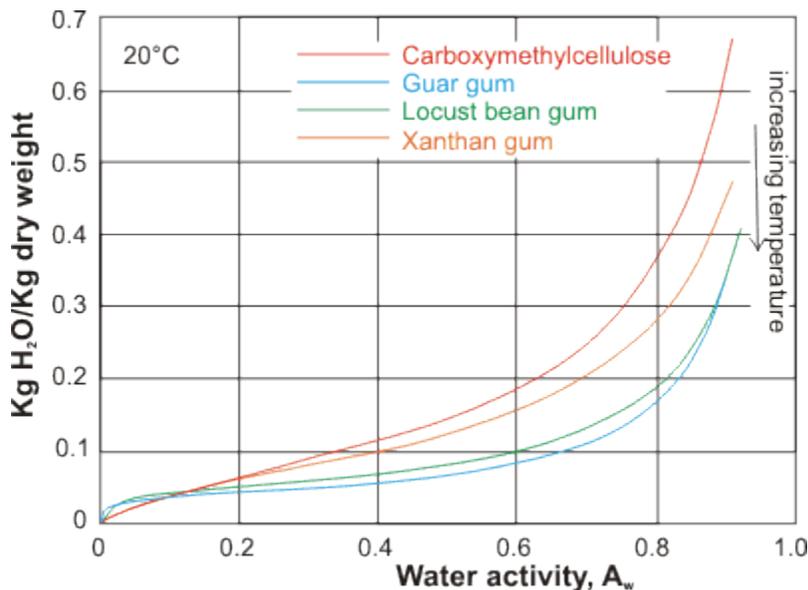


# Hydrocolloids and gums

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## Hydrocolloid polymers and gums

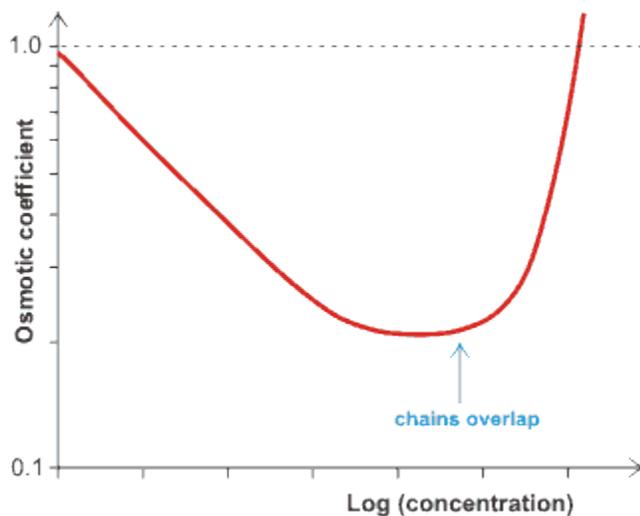
Hydrocolloids [227], often called gums,<sup>a</sup> are hydrophilic<sup>b</sup> polymers, of vegetable, animal, microbial or synthetic origin, that generally contain many hydroxyl groups and may be polyelectrolytes. They are naturally present or added to control the functional properties of aqueous foodstuffs. Most important amongst these properties are [viscosity](#) (including thickening and gelling) and water binding (see right [1815]) but also significant are many others including emulsion stabilization, prevention of ice recrystallization and organoleptic properties. The degree with which the hydrocolloid solutions mix with saliva, determined by their degree of chain entanglement, determines flavor perception [1050].

Other more specialist applications include adhesion, suspension, flocculation, foam stabilization and film formation. Foodstuffs are very complex materials and this together with the multifactorial functionality of the hydrocolloids has resulted in several different hydrocolloids being required; the most important of which are listed below.

- Agar (Jmol)
- Alginate (Jmol)
- Arabinoxylan (Jmol)
- Carrageenan (Jmol)
- Carboxymethylcellulose (Jmol)
- Cellulose (Jmol)
- Curdlan (Jmol)
- Gelatin (Jmol)
- Gellan
- $\beta$ -Glucan (Jmol)
- Guar gum (Jmol)
- Gum arabic
- Locust bean gum (Jmol)
- Pectin (Jmol)
- Starch (Jmol)
- Xanthan gum (Jmol)

Each of these hydrocolloids consists of mixtures of similar, but not identical, molecules and different sources, methods of preparation, thermal processing and foodstuff environment (for example, salt content, pH and temperature) all affect the physical properties they exhibit. Descriptions of hydrocolloids often present idealized structures but it should be remembered that they are natural products (or derivatives) with structures determined by stochastic enzymic action, not laid down exactly by the genetic code. They are made up of mixtures of molecules with different molecular weights and no one molecule is likely to be conformationally identical or even structurally identical (cellulose excepted) to any other. [[Back to Top](#) ▲]

## Properties of polyelectrolytes

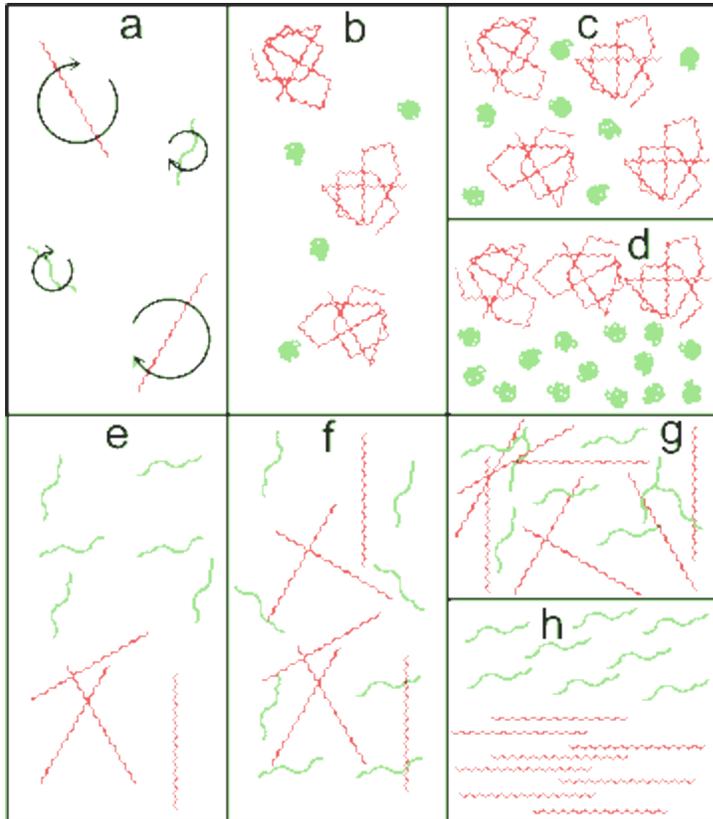


Many hydrocolloids are polyelectrolytes (for example [alginate](#), [carrageenan](#), [carboxymethylcellulose](#), [gum arabic](#), [pectin](#) and [xanthan gum](#)). The charged groups ensure strong hydration, particularly on a per-molecule basis. The presence of counterions and co-ions (ions with the same charge as the polyelectrolyte) introduce complex behavior that are ion-specific and depends on the concentrations of all ionic solutes [1473]. A proportion of the counterions remain tightly associated with the polyelectrolyte, being trapped in its electrostatic field and so reducing their activity and mobility; with the non-ideality of the solutions increasing on dilution down to very low levels as the associated proportion of the counterions increases. The behavior changes when the concentration of the polyelectrolyte necessitates the overlap of their structures [1493].

The [reduced viscosity](#) of such solutions increases on dilution as the polyelectrolyte chains stiffen. These properties of polyelectrolytes are more noticeable as the linear charge density (number of charged groups per unit length) increases. Properties of these solutions (such as enthalpy of dilution [1473]) are difficult to predict as small changes in the polyelectrolyte concentration, ionic strength or specific ions may result in large changes in the three-dimensional structure of the polyelectrolyte, including the possibility of the formation of [aqueous biphasic systems](#). [[Back to Top](#) ▲]

## Mixtures of hydrocolloids

Mixtures of hydrocolloids (gums) show such a complexity of non-additive properties that it is only recently that these can be interpreted as a science rather than an art. There is enormous potential in combining the structure-function knowledge of polysaccharides with that of the structuring of water. The particular parameters of each application must be examined carefully, noting the effects required (for example, texture, flow, bite, water content, stability, stickiness, cohesiveness, resilience, springiness, extensibility, processing time, process tolerance) and taking due regard of the type, source, grade and structural heterogeneity of the hydrocolloid(s).



Mixed hydrocolloids, at low concentrations (**a**), influence large volumes of water within their [radius of gyration](#). As the concentrations increase different scenarios are possible. Individual molecules may fold up to form globular structures (**b**). This entropy-driven process allows the retention of rotational freedom. Further concentration (**c**) may cause phase separation (**d**) due to the different influences on the water structuring.

More commonly, hydrocolloids retain their extended structures. This may give rise to mixed entanglement (**f**; rarer) or phase-separated entanglement (**e**, commoner). Mixed entanglement may give rise to gels (**g**) at higher concentrations. Phase separations may be entropy-driven as they may allow greater freedom of movement due to the similarity in the molecular shapes (**h**).

Sometimes junction-zones arise, forming gels.

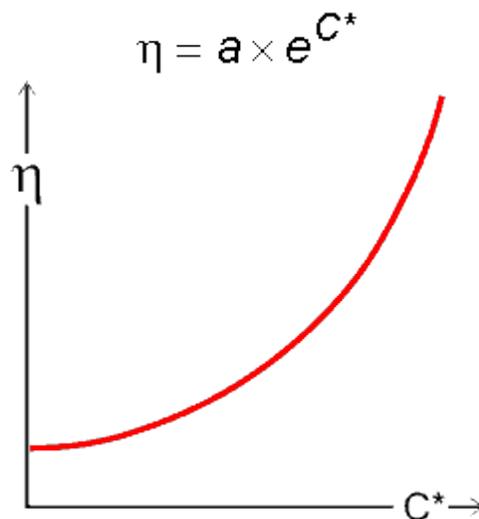
All [hydrocolloids interact with water](#), reducing its diffusion and stabilizing its presence. Generally neutral hydrocolloids are less soluble whereas polyelectrolytes are more soluble but hydration kinetics depends on many factors; xanthan, guar and carboxymethylcellulose are soluble in cold water but carrageenan, locust bean gum and many alginates require hot water for complete hydration. Such water may be held specifically through direct hydrogen bonding or the structuring of water or within extensive but contained inter- and intra-molecular voids. Interactions between hydrocolloids and water depend on [hydrogen bonding](#) and therefore on temperature and pressure in the same way as [water cluster](#) formation.

Similarly, there is a reversible balance between entropy loss and enthalpy gain but the process may be kinetically limited and optimum networks may never be achieved. Hydrocolloids may exhibit a wide range of conformations in solution as the links along the polymeric chains can rotate relatively freely within valleys in the [potential energy landscapes](#). Large, conformationally stiff hydrocolloids

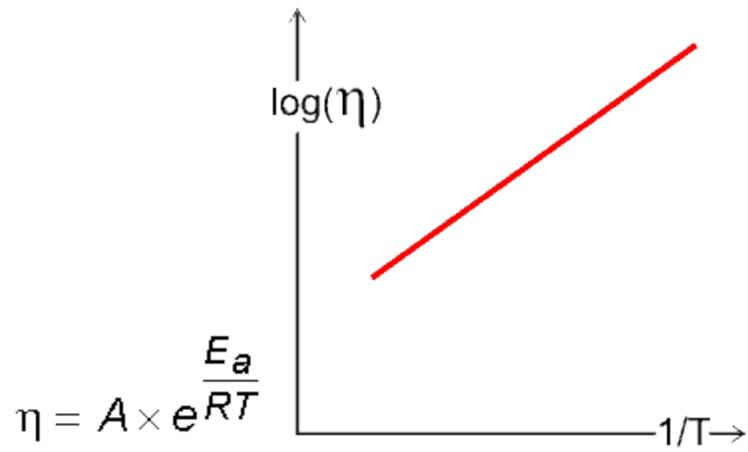
present essentially static surfaces encouraging extensive structuring in the surrounding water. Water binding affects texture and processing characteristics, prevents [syneresis](#) and may have substantial economical benefit. In particular, hydrocolloids can provide water for increasing the flexibility (plasticizing) of other food components. They can also effect ice crystal formation and growth so exerting a particular influence on the texture of frozen foods. Some hydrocolloids, such as [locust bean gum](#) and [xanthan gum](#), may form stronger gels on freeze-thaw due to kinetically irreversible changes consequent upon forced association as water is removed (as ice) on freezing [\[468\]](#). [[Back to Top](#) ▲]

## Effect on viscosity

As hydrocolloids can dramatically affect the flow behavior of many times their own weight of water, most hydrocolloids (gums) are used to increase viscosity (see [rheology page](#)), which is used to stabilize foodstuffs by preventing settling, phase separation, foam collapse and crystallization. Viscosity generally changes with concentration, temperature [\[236\]](#) and [shear strain rate](#) in a complex manner dependent on the hydrocolloid(s) and other materials present; mixtures of hydrocolloids may act synergically to increase viscosity or antagonistically to reduce it. These changes may generally be fitted to equations such as:

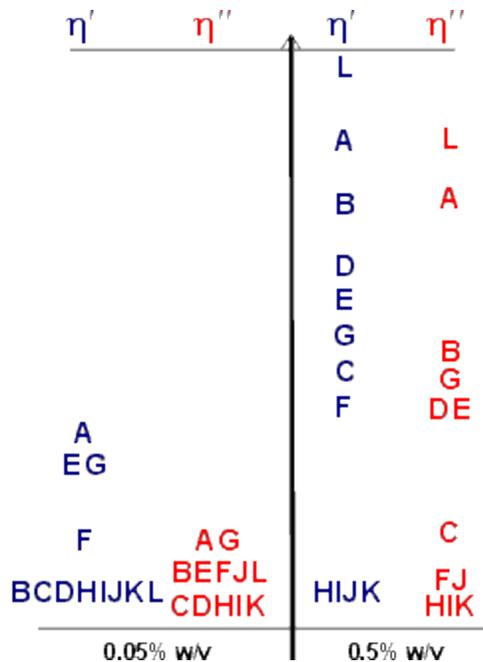


where  $\eta$  is the viscosity,  $a$  is pre-exponential factor and  $C^*$  is the concentration in units specific for the circumstances; often about 1% wt/vol.



where  $\eta$  is the viscosity,  $A$  is pre-exponential factor and  $E_a$  is a constant (known as 'activation energy' from the similarity with the Arrhenius equation),  $R$  is the gas constant and  $T$  is the absolute temperature.

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Unfortunately these equations cannot be combined as the specific concentration units change with temperature. Their non-linear nature means that extreme care should be taken when investigating possible synergistic relationships.

The relative viscosities of the more important hydrocolloids are influenced by their molecular weight distribution and other structural properties, dependent on their source and preparatory methodology, but are approximately as shown opposite;

A [carboxymethylcellulose](#), B [Guar](#), C [locust bean gum](#), D [κ-carrageenan](#), E [λ-carrageenan](#), F [ι-carrageenan](#), G [xanthan](#), H [gum arabic](#), I [pectin](#), J [microcrystalline cellulose](#), K [methylcellulose](#), L [konjac mannan](#).

The viscous ( $\eta'$ ) and elastic ( $\eta''$ ) components of the (complex) viscosity ( $\eta^*$ ) of the gums, at 0.05% w/v and 0.5% w/v, are compared at 4 °C and 50 s<sup>-1</sup> [using data from [694](#)] where  $\eta^* = \eta' + i\eta''$ .

Many hydrocolloids also gel, so controlling many textural properties. Gels are liquid-water-containing networks showing solid-like behavior with characteristic strength, dependent on their concentration, and hardness and brittleness dependent on the structure of the hydrocolloid(s) present.

Hydrocolloids display both elastic and viscous behavior where the elasticity occurs when the entangled polymers are unable to disentangle in time to allow flow. Mixtures of hydrocolloids may act synergistically, associating to precipitate, gel or form incompatible [biphasic systems](#); such phase confinement affecting both viscosity and elasticity.

Hydrocolloids are extremely versatile and they are used for many other purposes including (a) production of [pseudoplasticity](#) (that is, fluidity under shear) at high temperatures to ease mixing and processing followed by thickening on cooling, (b) liquefaction on heating followed by gelling on cooling (for example, cold set gels like [agarose](#), [gellan](#) and [carrageenan](#)), (c) gelling on heating to

hold the structure together (for example, thermogelling heat set gels such as [ascurdlan](#) and [methyl cellulose](#)), (d) production and stabilization of multiphase systems including films.

Atomic force microscopy has been used to clarify the network structures on gelling, and gives useful results so long as care is taken that the structures do not change during preparation [[1242](#)]. [[Back to Top](#) ▲]

## Hydrocolloid action

These properties of hydrocolloids must be due, both singly and in concert, to their structural characteristics and the way they interact with water. For example:

- Hydrocolloids gel when intra- or inter-molecular hydrogen bonding (and sometimes salt formation) is favored over hydrogen bonding (and sometimes ionic interactions) to water to a sufficient extent to overcome the entropic cost. Often the hydrocolloids exhibit a delicate balance between hydrophobicity<sup>b</sup> and hydrophilicity. Extended hydrocolloids tend to tangle at higher concentrations and similar molecules may be able to wrap around each (forming helical junction zones) other without loss of hydrogen bonding but reducing conformational heterogeneity and minimizing hydrophobic surface contact with water so releasing it for more energetically favorable use elsewhere. Under such circumstances a minimum number of links may need to be formed (that is, a junction zone which, if helical, generally requires a complete helix) to overcome the entropy effect and form a stable link. Where junction zones grow slowly with time, the interactions eliminate water and syneresis may occur (as in some jam and jelly).
- Polysaccharide hydrocolloids stabilize emulsions (see [[1501](#)]) primarily by increasing the viscosity (slowing the thermodynamically favored breakdown of the emulsion) but may also act as emulsifiers, where their emulsification ability is reported as mainly being due to accompanying (contaminating or intrinsic) protein moieties [[309](#)]. In particular, electrostatic interaction between ionic hydrocolloids and proteins may give rise to marked emulsification ability with considerable stability so long as the appropriate pH and ionic strength regime is continued. Denaturation of the protein is likely to lead to improved emulsification ability and stability.
- Mixtures of hydrocolloids may avoid self-aggregation at high concentration due to structural heterogeneity, which discourages crystallization but encourages solubility. Hydrocolloids may interact with other food components such as aiding the emulsification of fats, stabilizing milk protein micelles or affecting the stickiness of gluten.
- The particle size of hydrocolloids and its distribution are important parameters concerning the rate of hydration and emulsification ability.
- Negatively charged hydrocolloids change their structural characteristics with counter-ion type and concentration (including pH and ionic strength effects); for example, at high acidity the charges disappear and the molecules become less extended.
- Physical characteristics may be controlled by thermodynamics or kinetics (and hence processing history and environment) dependent on concentration. In particular these may change with time in a monotonic or oscillatory manner.
- Different hydrocolloids prefer [low-density or higher density water](#) and other hydrocolloids show compatibility with both. As more intra-molecular hydrogen bonds form so the hydrocolloids become more hydrophobic and this may change the local structuring of the

water. Mixed hydrocolloids preferring different environments produce 'excluded volume' effects on each other's effective concentration and hence [rheology](#).

- In the glassy state, conformational changes are severely inhibited, but the water held by hydrocolloids may act as plasticizer (allowing molecular motion) greatly reducing the glass transition temperature by breaking inter-molecular hydrogen bonding.

Hydrocolloids, together with other dietary fiber, are increasingly being seen as contributing to a healthy diet, having a number of positive [health benefits](#). Although this site concentrates on food aspects, hydrocolloids also have many other major economic uses such as in the chemicals, oil and cosmetic industries. [[Back to Top](#) ▲]

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## Footnotes

<sup>a</sup> Some hydrocolloids are not gums and some gums are not hydrocolloids. Notably amongst the latter are 'chewing gums' and many gum adhesives, which are water-insoluble rubbery materials. [[Back](#)]

<sup>b</sup> **Hydrophilic** solutes (that is, solutes or structures possessing hydrophilicity) interact with water with greater or comparable strength to water-water interactions whereas **hydrophobic** solutes (that is, solutes or structures possessing hydrophobicity) only weakly interact with water with strength far less than water-water interactions. [[Back, 2](#)]

Source : <http://www1.lsbu.ac.uk/water/hydro.html>