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Colloidal Stability of Cellulose Suspensions

Marina Stygar Lopes

Abstract

Cellulose is the most abundant natural compound in nature and the main component of the cell wall of plants. It is a linear polymer with a high degree of polymerization, responsible for most of the properties of wood. Colloidal phenomena are often used in various industrial production processes. Suspended cellulose, used worldwide in the paper and cellulose industries, with regard to stability, has a high tendency to aggregate and form clots. The different interactions between the dispersed phase and the dispersion phase are one of the critical points in the study of the behavior and stability of colloids. Cellulose is no different, as several studies seek to improve the colloidal stability of cellulose in aqueous media by observing the specific characteristics of the colloid, such as its geometry, mass and area/volume ratio, and the possible interactions between particles that make up the cellulose dispersion in order to understand and control colloidal stability. Therefore, the objective of this chapter is to define the main characteristics of colloids, to classify them, to present the main methods of preparation, to address important aspects about colloid stability and the colloidal stability of cellulose.

Keywords: colloids, suspension, cellulose, colloidal stability, cellulose fibers, lignocellulosic material

1. Introduction

Colloids are heterogeneous mixtures of at least two distinct phases, with the material of one of the phases in a finely divided form (solid, liquid or gas), called dispersed phase, mixed with the continuous phase (solid, liquid or gas), called medium dispersion [1].

Understanding and controlling the stability of colloidal dispersions is essential for its satisfactory use. For both economic and environmental reasons, water is often required as a dispersing phase, even when the particles that need to be kept in suspension are hydrophobic, as is the case with cellulose [1].

Cellulose has been gaining importance in the industrial scenario due to the growing interest in sustainability and environmental protection, becoming a competitive material since it is renewable, abundant, low cost, non-petroleum and non-toxic [2].

Suspended cellulose has a tendency to aggregate. In this way, some strategies to avoid cellulose self-agglomeration in aqueous medium have been used in order to reduce the hydrophilic character of cellulose, avoiding the formation of additional hydrogen bonds between cellulose fibers [3].

Therefore, this chapter aims to contribute to the field of study of colloids and their characteristics, in addition to cellulose with regard to its characteristics and behavior of aqueous solutions of cellulose and alternatives sought to improve the colloidal stability of cellulose suspensions.

2. Colloids

Colloids are systems formed by macromolecules or particles dispersed in a medium, in which one or more components have at least one of their dimensions within the range of 1 nm to 1000 nm [4].

Colloidal systems have been used since the dawn of humanity. Ancient people used gels from natural products as food, clay dispersions for the manufacture of ceramic utensils and colloidal pigment dispersions to decorate cave walls [5].

Colloidal systems are present in our daily lives in several products and technologies, such as personal hygiene (shampoo, toothpaste, foam, shaving cream, makeup, cosmetics) and in food (milk, coffee, butter, vegetable creams, fruit jellies, beer, soda or ice cream). During a single day we are consuming several colloids [5]. Colloids are also present in several consumer goods production processes, including drinking water, in the separation processes in the biotechnology industries and in the treatment of the environment.

In addition, colloidal phenomena are frequently used in industrial processes for the production of polymers, detergents, paper, soil analysis, food products, fabrics, precipitation, chromatography, ion exchange, flotation and heterogeneous catalysis. In orthomolecular therapeutic medicine, knowledge of the properties of colloidal systems can assist in the elucidation of diseases, such as Alzheimer's and Parkinson's [5].

2.1 Colloid characteristics

The factors that most contribute to the characteristics of a colloid are:

- The particle dimensions;
- The shape and flexibility of the particles;
- Surface properties;
- Particle-particle interactions;
- Particle-solvent interactions.

Colloids have specific characteristics such as high mass, high particle area/volume ratio and are relatively large. On the separation surfaces (interfaces) between the dispersed phase and the dispersion medium, characteristic surface phenomena are manifested, such as adsorption and double electrical layer effects, phenomena of great importance in determining the physicochemical properties of the system as a whole [6].

Depending on the affinity between the particles of a dispersion and the medium in which they are dispersed, we can classify colloids in two ways: lyophilic and lyophobic colloids. Lyophilic colloids are those in which the particle surface has an affinity for the solvent, keeping the dispersion more stable and minimizing aggregation. Lyophobic colloids, on the other hand, are those in which the particles have greater interaction with each other, which ends up leading to a rapid aggregation process [7].

2.2 Colloid classification

Regarding the colloid classification, there are the following categories:

- Aerosol: consists of a solid or a liquid dissolved in a gas.
- Foam: consists of a gas dispersed in solid or liquid.
- Emulsion: are colloids formed by liquid dispersed in another liquid.
- Sol: are colloids formed by the dispersion of a solid in a liquid or solid.
- Gel: solid of gelatinous material formed from a colloidal dispersion, in which the dispersed is in the liquid state and the dispersant in the solid state.

The **Table 1** shows some different types of colloids according to the state of the continuous and dispersed phases, and examples found in everyday life.

| | | Scattered | | |
|------------|--------|---|---|---|
| | | Gas | Liquid | Solid |
| Dispersant | Gas | Does not exist. All gases are soluble with each other | Aerosol Liquid Examples: cloud, fog | Aerosol solid Examples: smoke, dust in suspension |
| | Liquid | Liquid foam Example: soap foam, shaving cream, whipped cream | Emulsion Examples: milk, honey, mayonnaise, creams | Sol Example: paints, colored glass |
| | Solid | Solid foam Example: pumice, expanded polystyrene | Gel Examples: gelatin, cheese, jam | Solid Sun Example: ruby and sapphire crystal, metal alloys |

Table 1.
 Classification of colloids according to the dispersed phase and dispersion medium.

Colloidal systems can be divided into three types: colloidal dispersions, true macromolecule solutions and association colloids [8].

Colloidal dispersions are heterogeneous systems composed of two or more phases, as shown in **Table 1**, and these systems are thermodynamically unstable, due to their high surface free energy. In a colloidal dispersion, the interfacial area of the dispersed phase is very large, which requires a lot of energy to keep it dispersed. In an attempt to minimize the free energy of the surface, the system tends to minimize the area, based on the aggregation of the dispersed phase [8].

True macromolecule solutions are thermodynamically stable colloidal systems, that is, they will not separate phase. Polymeric solutions are examples of this class of colloids. Association colloids, which are also thermodynamically stable, are formed by the association of surfactant molecules, that is, micellar aggregates [8].

2.3 Colloid preparation

For the production of colloids there are two groups with different production methods, they are: dispersion methods and condensation methods [3].

2.3.1 Methods of dispersion

Mechanical spraying: for the production of colloids a solid substance is used added to a liquid, using colodal mills, which is a method used in the industry for the production of colloidal pigments.

Electric spraying: produced using the Bredig method, in which two electrodes are immersed in water to generate an arc. Spraying results in a coarse suspension from the metal particles. In the suspension you get the hydrosol. Electric spraying is used in the production of metallic colloids. In the reaction of substances such as benzene and ethyl ether, alkaline and alkaline earth colloids are produced.

Spraying by Ultrasound: from mechanical vibrations, which can be produced under a piezoelectric quartz generator in an excitation process, the formation spray of colloidal solutions is generated.

Peptization: performed with peptizing agents that have the ability to disintegrate, with colloids as the final product. These materials are used, for example, in the food industry in the production of gelatins, gums, and agar from the use of hot water, which is a peptizing agent.

2.3.2 Condensation methods

The condensation method is a means of producing colloids carried out with the precipitation of an insoluble substance by means of a chemical transformation between solvent substances. During its chemical transformation, the insoluble product is in the molecular state, occurring after condensation.

2.4 Stability of colloids

The different interactions between the dispersed phase (particles) and the dispersion phase (continuous) constitute one of the critical points in the study of the behavior and stability of colloids. The interactions between the particles that make up a dispersion and the dispersing medium are fundamental to understand colloidal stability [9].

The stability of a dispersion can be thermodynamic or kinetic and one of the ways to understand the difference between them is in terms of the colloid stabilization time. While a thermodynamically stable colloid will remain unchanged for an infinite time, maintaining properties like temperature and concentration unchanged, kinetically stable colloids tend to aggregate over time. Therefore, the study of colloidal chemistry makes it possible to change the time in which the colloid remains kinetically stable [8].

When it comes to particles, the energy in van der Waals' interactions comes from integrating the potential of all the molecules that make it up [10]. Van der Waals interactions between two particles will always be attractive if the particles are made of the same material, no matter what medium they are in [11]. If the particles are different in nature, van der Waals interactions can be attractive or repulsive [12]. In the study of colloidal dispersions, the focus is mostly on the interaction of particles of the same nature, that is, they are attractive interactions [13].

To increase the stability of a colloidal dispersion the steric effect of macromolecules is used to prevent the particles from aggregating by adding a stabilizer that will adsorb on the surface of the particle [13]. If the adsorbed macromolecule is in a good solvent, its chains expand. When it encounters a chain from another particle, there is a restriction in the conformation of both chains in the volume between the two particles, causing a decrease in configurational entropy and an

increase in free energy [14]. To minimize this effect, the chains of the macromolecules repel each other, causing a repulsive effect between the particles, preventing aggregation.

Regarding the stability of aqueous colloidal dispersions, they are sensitive to the presence of electrolytes and polyelectrolytes (charged polymers of high molecular mass), since the colloidal particles can irreversibly aggregate in the presence of electrolytes and result in large and compact aggregates (clots) by a process called coagulation, while in the presence of polyelectrolytes there may be the formation of less dense aggregates (flocules), which can be easily broken and dispersed by mechanical agitation [15].

Understanding and controlling the stability of colloidal dispersions is essential for its satisfactory use. Some specific applications require that such dispersions be maintained over a wide range of temperatures and chemical conditions [8].

For both economic and environmental reasons, water is often required as a dispersing phase, even when the particles that need to be kept in suspension are hydrophobic. Water is a highly structured material, due to the hydrogen bonds that connect the molecules to each other. In the vicinity of a hydrophobic surface, ruptures of the hydrogen bonds between water molecules occur, increasing the free energy in relation to the solution. As a consequence, water is expelled to regions more favorable to hydrogen bonding. The migration of water molecules results in a mutual attraction between hydrophobic surfaces that implies a reduction in the free energy of the system [11].

3. Cellulose

Cellulose has stood out in the last 20 years as a study material for several applications, as it is the most abundant, renewable and natural polymer on the face of the Earth [15], and can be found mainly in woody plants (wood), annuals and in grasses [16]. Cellulose is located mainly in the secondary cell wall, corresponding to approximately 40 to 45% of the wood mass [17].

Cellulose ($C_6H_{10}O_5$)_n is a polysaccharide, linear chain containing from hundreds to thousands of chemical bonds involving carbon, hydrogen and oxygen atoms (**Figure 1**) [18]. The cellulose chain is of high molecular weight, which tends to form hydrogen bonds between the molecules [19, 20]. The hydroxyl groups of cellulose molecules form hydrogen bonds that can be intramolecular or intermolecular,

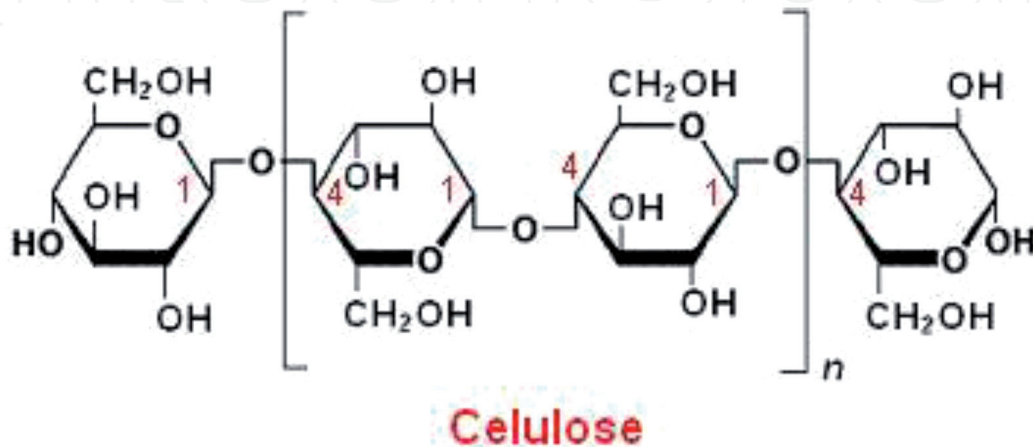


Figure 1.
Chemical structure of cellulose.

directing the crystalline packaging, and it is these bonds that make cellulose a stable polymer and appreciated as reinforcement in composites [21, 22].

Its organized structure is formed by cellulose microfibrils, which due to intermolecular bonds form the fibrils, which in turn are composed in an orderly fashion in order to form cellulosic fibers. Cellulose fibers are made up of two regions, the crystalline region, in which the microfibrils are presented in an extremely orderly manner, and the amorphous region, in which they are arranged in a less ordered manner [17], and for some lignocellulosic sources the amorphous regions can reach 50% of the structure [22].

Despite the hygroscopic nature of the individual cellulose molecules, the absorption of water molecules is only possible in the amorphous zones, since there is a lack of empty spaces in the crystalline structure. Hydroxy groups are the most abundant groups in the cellulose molecule, followed by the acetal bonds that form the ring of pyranoses [23].

In the crystalline regions of cellulose, we also have that the intra and intermolecular interactions can vary, giving rise to the various polymorphs [18]. The degree of polymerization and the crystallinity of cellulose vary according to the lignocellulosic source [1]. Due to the presence of crystalline and amorphous regions, cellulose can be classified as a semicrystalline fibrillar material [24].

Using cellulosic materials has several advantages, such as: its low cost, low density, high mechanical resistance and high elastic modulus. Due to the stable structure of their crystalline regions, cellulose fibrils have high mechanical properties along the longitudinal direction [24]. It is also possible to benefit from the high stiffness of the cellulose crystal which, when used on a nanometer scale for the production of composite materials, makes it possible to preserve the optical properties of the original material while improving the mechanical properties [25].

3.1 Colloidal stability of cellulose

Cellulosic pulp is a material whose characteristics and properties are determined by its origin. Cellulose modification methods are used when carrying out processes carried out in an aqueous medium, but cellulose is an amphiphilic polymer, that is, it presents a hydrophilic region that dissolves in water, and another hydrophobic region that does not dissolve in water, due to the presence of crystalline and amorphous regions.

The geometry, size and surface density of the particles are also properties that interfere with the processes of coagulation and flocculation. The polymers used with water retention agents increase the forces of colloidal attraction and induce flocculation through different mechanisms, based on different effects. We can mention: flocculation by bridge effect, flocculation by depletion effect and flocculation by reinforced bridge effect [1].

In the case of cellulose fibers, these properties are not well defined due to the variety in the size and shape of the fibers. However, it is known that cellulose fibers when dispersed in water have a pH of around 6, which indicates the acidic character of the surface, therefore a tendency to preferentially adsorb OH⁻ group. In this way, the aqueous dispersions of cellulose fibers are influenced in their colloidal stability by the presence of a double electrical layer under their surface, resulting from the dissociation of different functional groups, such as carboxylics [26].

The pure cellulose fiber in suspension has a high tendency to aggregate and form clots by the action of gravity. However, studies show that through the addition of symmetrical or asymmetric electrolytes the tendency to coagulate the cellulose fiber suspension can be maximized or minimized depending on the final objective. The addition of cationic starch and calcium carbonate to the cellulose fiber suspension

causes a change in the charge signal of the fiber surface, resulting in phenomena of fiber-fiber interaction that guarantees greater stability in relation to pure cellulose fiber [1].

3.2 Cellulose used in paper production

In the refining process, for example for the production of paper, cellulose fibers are immersed in water. The fibrils, which make up the cells, are composed of crystalline regions that, when immersed in water, absorb a quantity of this water across all exposed crystalline surfaces, causing their swelling and decreased attraction between the fibrils. The mechanical action of shearing the fibers through refiners speeds up this swelling, as it exposes the surfaces previously located inside the fibers, causing an increase in surface exposure, which promotes a greater number of contacts and connections between the fibers, resulting in this stronger paper [1].

The steps of converting cellulose to paper involve many surface chemical interactions, interactions between fibers and colloidal particles. Understanding these interactions is useful for product development and improving the resolution of operational problems.

4. Conclusions

This chapter sought to define the main characteristics of colloids, as well as their classification, methods of preparation and finally to address characteristics of colloid stability. Cellulose, the most abundant biopolymer in the world, is a colloid widely used in several industries. This colloid proves challenging for some segments due to its detailed characteristics throughout of the chapter. Studies continue to be carried out on this topic in order to bring solutions to improve the colloidal stability of cellulose.

Notes/Thanks/Other declarations

I thank IntechOpen for the opportunity and the Federal University of Paraná for my training from undergraduate to doctorate.

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