EFFECT OF THE ADDITION OF A CATIONIC DERIVATIVE OF THE NATURAL POLYSACCHARIDE GUAR GUM ON THE STABILITY OF AN AQUEOUS DISPERSION OF ALUMINA

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ABSTRACT

In the present work, the action of a cationic polyelectrolyte (the ammonium hydroxy-propyl-trimethyl chloride of the polysaccharide guar gum, commercially know as cosmedia guar, CG) in aqueous alumina suspension was investigated. This polymer was used aiming to find alternatives for synthetic polymers, as for instance, sodium polyacrylate−PANa, normally used as a deflocculant agent of alumina suspension. Due to its positive charge, this polyelectrolyte (CG) can have electrostatic attractive interactions with the negative charges present on the surface of alumina in alkaline pH. Besides, the presence of hydroxyl groups in this polymer enables attractive interactions with alumina, by means of hydrogen bonds, thus preventing the approximation of other particles and leading to steric stabilization, as occurs when electrostatic attractive interactions (CG/alumina) are present. The study was carried out using the Fiber Optic Quasi-Elastic Light Scattering (FOQELS) technique, aiming to determine particle size. The results obtained with this technique were correlated mainly with those obtained by viscometry. The measurements of particle size, as a function of time, showed that the addition of this

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polyelectrolytic macromolecule (CG) keeps the particles dispersed for a longer time, in comparison with the suspension containing only alumina.

Key Words: Alumina suspension; Steric stabilization; Cosmédia guar; Cationic polyelectrolyte

INTRODUCTION

Depending on their application, ceramic pieces can be either porous or dense. However, aqueous suspensions with high oxide concentration are normally used, which renders the control of their properties difficult. Many applications require that the particles be maintained dispersed in suspension. As a result, organic additives are largely used in colloidal processing of ceramic powders, to control interparticle forces, as well as to prevent the aggregation of primary particles.[1] Polyacrylic acid and citric acid stand out among the additives most used in the ceramic industry.[2]

When polymers are used to obtain stable suspensions, flocculation or deflocculation efficiency depends on the nature of the polymer and of the substrate, the quantity of polymer adsorbed, the configuration of the solid/liquid interface, and also on the solvent properties.[3]

In a system with a high concentration of solids, the attractive interaction among its particles increases with the decrease in their size. Therefore, the random movement of the colloidal particles, resulting from the impact of the molecules of the liquid with them, that is, the Brownian movement, leads to particle-particle collisions, which in turn leads to the formation of agglomerates. One of the main forces causing particle agglomeration in systems with high solid concentration is the attractive forces of van der Waals. Besides, the presence of electric charges in any interface gives rise to electric effects, which in many cases determine the characteristic of this interface to a large extent.[4]

Particles can acquire surface electrical charge in contact with a polar environment, as water, for example, as a result of mechanisms which can involve ionization or ionic adsorption. This surface charge, together with the molecular thermal motion, leads to the formation of the Electrical Double Layer (EDL). [5−7]

The three most important kinds of stabilization mechanisms of aqueos suspension are:

Electrostatic: a charge is developed in the solid-liquid interface leading to the formation of a diffuse electrical double-layer (EDL) surrounding each particle. The interactions of these electrical double layers keep the particles separated by rising the mutually repulsive forces;
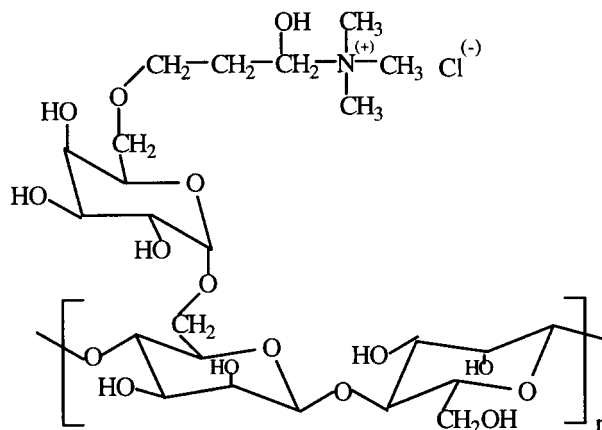
Figure 1. Chemical structure of cosmedia guar (CG).

Steric stabilization, which is due to the adsorption of a polymeric layer on the surface of the particles. Stabilization results from the repulsion between these particles caused by the adsorbed polymeric layer on the particles;

Electrosteric stabilization, which is a combination of the two previous mechanisms.[8,9]

An oxide particle, as for example alumina, one of the most used oxides in the ceramic industry, acquires negative, positive surface sites when in contact with a liquid environment (normally aqueous) through the reaction of the hydroxyl group of its surface. When the ions that determine the surface potential are $H^{(+)}$ and $OH^{(-)}$, the surface net charge depends on the pH of the environment.[10]

Then, it is possible to have negative, positive and neutral sites in almost all the pH range. However, depending on the pH, the net charge will be negative, positive or equal to zero. At a specific pH, the number of negative and positive charges is equal and we have the point of zero charge (PZC). The point of zero charge of alumina normally changes in the range of pH values from 6.0 to 8.5.[13−15]

In the present work, the action of a cationic polyelectrolyte, the ammonium hydroxi-propyl-trimethyl chloride of the polysaccharide guar gum, commercially know as cosmedia guar (CG, Fig. 1), in aqueous alumina suspension was investigated. Guar gum is a natural carbohydrate polymer, consisting of a polymannan backbone with single galactose unit side chains.[16,17]

Cosmedia guar keeps its polyelectrolytic property in the whole range of pH, because the groups that lend it a positive charge, is a quaternary amine. This polymer was used aiming to find alternatives for synthetic polymers, as for instance, sodium polyacrylate−PANa, normally used as a deflocculant agent of alumina suspension.[18,19] Due to its positive charge, this polyelectrolyte (CG) can have attractive interactions with the negative charges

present on the surface of alumina in alkaline pH. Besides, the presence of hydroxyl groups in this polymer enables attractive interactions with alumina, by means of hydrogen bonds, thus preventing the approximation of other particles and leading to steric stabilization, as occurs when electrostatics attractive interactions (CG/alumina) are present.

The study was carried out using the Fiber Optic Quasi-Elastic Light Scattering (FOQELS) technique, aiming to determine particle size. This technique uses photon correlation spectroscopy (PCS) of quasi-elastically scattered light (QELS), which is based on correlating the fluctuations of the average, scattered, laser light intensity.[20] The results obtained with this technique are correlated mainly with those obtained by viscometry.

EXPERIMENTAL

Materials

The alumina powder used in this study, APC-3017G density $3.9 \, g \, cm^{-3}$, average particle size of $2.5 \, \mu m$, was generously given by Alcoa Aluminio AS (Brazil). The cationic polyelectrolyte used (the ammonium hydroxi-propyl-trimethyl chloride of guar gum, commercially known as cosmedia guar— CG) was courtesy of Henkel (Brazil). Its molecular weight, as informed by the supplier, is $200,000 \, g/mol$. A 10-$g \, dm^{-3}$ solution was prepared under stirring during 10 min, at $80°C$, and then at room temperature during 12 hr. For some experiments, these solutions were submitted to ultrasound by sounding it (Branson Sonifier 450) with a 40% pulse and intensity of 5, in varying times.

Methods

Viscosity measurements were performed using a Brookfield Visco-meter−model DV II using spindle 2 and 3 rpm, at room temperature. Aqueous alumina suspensions (578 g/alumina in 315 mL/water, 64 wt%) were prepared and stirred during 1 hr. In another set of experiments, the suspension was stirred at various times, up to 5 hr, but no significant difference was observed in the viscosity of the suspension. Then, the suspensions were stirred during 1 hr in all the experiments described in this work. The pH of aqueous alumina suspension was adjusted with the addition of solutions of HCl $1 \, mol \, dm^{-3}$ and NaOH $1 \, mol \, dm^{-3}$. A similar procedure was used when Cosmedia guar was added to the suspension.

Particle sizes were measured by Photon Correlation Spectroscopy (PCS) using a Brookhaven Instrument (50 mW, $\lambda = 532$ nm neodymium laser). This apparatus makes accurate measurements in the order of the particle size of 2 to 2,000 nm. For these measurements, polymer solutions were added to
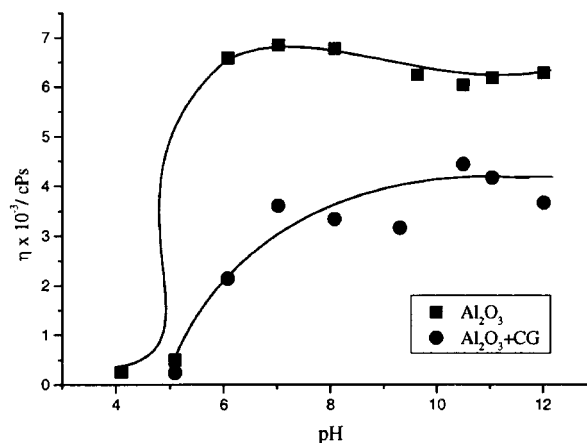
Figure 2. Viscosity of aqueous suspension of alumina and alumina/CG as a function of pH, without ultrasound effect, 3 rpm, spindle 2.

diluted suspensions of alumina (2 wt%). These suspensions were stirred during 1 hr, just before measurements. In another set of experiments, the samples were also sonicated during 5 min, using an ultrasound bath just before the experiment. An aliquot of approximately 3.0 mL was put into the appropriate sample vessel and introduced into the apparatus for measurement. Particle size measurements are promptly readable on the display.

RESULTS AND DISCUSSION

Figure 2 shows the viscosity as a function of pH, for the alumina suspension with and without cosmedia guar. Previously, the viscosity of the alumina suspension was measured as a function of the quantity of CG solution (10 g dm^{-3}) added. It was observed that the addition of 30 mL of this solution to the suspension containing 578 g/alumina in 315 mL/water, carried to the lowest viscosity value. Therefore, this volume was used in all the experiments.

The alumina used in the present study has the point of zero charge (PZC) near pH 8.0, as determined by zeta potential (figure not shown).[21] This value is in agreement with those found in the literature.[22,23] The PZC is usually a characteristic of the solid surface and represents the point at which the oxide surface contains an equal number of positive and negative charges, and therefore attractive particle interactions are predominant at this point.[24,25]

For the alumina and the alumina/CG suspensions, in the pH range of 4.0−5.0, low values of viscosity are observed, due to the repulsive interactions between the alumina particles themselves, mostly charged positively in this pH range, leading to electrostatic stabilization. Over pH 5, the
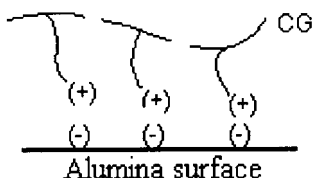
Figure 3. Possible interactions on CG/alumina surface at alkaline pH.

alumina/CG suspension presents a lower value of viscosity in the entire pH range, in comparison to the alumina suspension. This probably occurs due to the interaction between the positively charged macromolecules and the alumina surface, which in an alkaline medium presents mostly negative sites. Considering that CG is a branched polyelectrolyte, it can be proposed that probably the interaction CG/alumina surface, on alkaline pH range, occurs due to a single site attachment of CG on alumina surface, as it is schematically shown in Fig. 3. These interactions lead to stabilization through electrosteric mechanism.

Seeking a larger decrease in viscosity due to the interaction alumina/CG, it was attempted to reduce the cosmedia guar chain size, submitting it to ultrasound, using a system in which the sound is introduced into the CG solution. Smaller chains can be adsorbed more easily on the particle surface, hindering their aggregation. Larger chains can interact with several particles at one time, which may lead to flocculation by the bridge mechanism.[15]

Figure 4 shows the decrease in viscosity for the CG solution, as a function of ultrasound application time, indicating that there was a decrease in its macromolecular size. However, the addition of these smaller chains to the alumina suspension did not lead to a significant improvement on the action of this macromolecule as a stabilizing agent of the alumina suspension, as observed in Fig. 5.

In Fig. 5, a low viscosity in the pH range 4.0−5.0 can be observed. In this range, the alumina particles present a larger number of positive sites, and therefore, there is electrostatic repulsion, that is, there is repulsion between the positively charged alumina particles themselves, and consequently, these viscosity values, the lowest ones, are a consequence of the electrostatic repulsion between the alumina particles.

An increase in viscosity could take place if there was not any adsorption of the polymer on the surface of the alumina particle, since the viscosity increases when the polymer is free in the solution. However, from Fig. 5, it is observed that besides the electrostatic repulsion (alumina−alumina repulsion), the adsorption of the macromolecule on the surface of alumina probably occurs, due to attractive interactions, probably involving hydroxylic groups of the macromolecule and the alumina surface, mainly through hydrogen bonds.
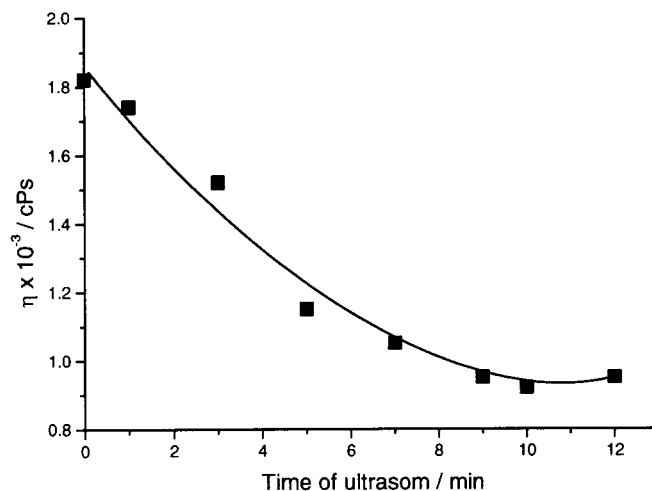
Figure 4. Viscosity as a function of ultrasound treatment time for the CG solution (10 g/L), pH 9.5, 3 rpm, spindle 2.

Table 1 presents the values of particle diameter size, in suspension, determined by particle size analyzer—Fiber Optical Quasi-Elastic Light Scattering—FOQELS for alumina (the particle size of the dry solid alumina is presented in the Experimental part). The suspensions (alumina/CG) were also submitted to ultrasound during 5 min. The beaker containing the suspension was put in a bath and submitted to ultrasound effect. The measurements were made immediately after the sample vessel was placed inside the apparatus, which meant t = 0, in relation to the results reported in the next item. pH 8 was chosen because it is near the pH_{pzc} of the alumina used in the present work.
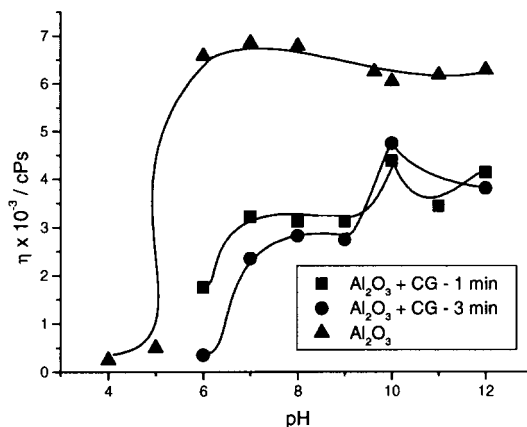

Figure 5. Viscosity as a function of pH for the alumina/CG suspension (30 mL of 10 g/L CG solution). CG solution previously submitted to different ultrasound times, 3 rpm, spindle 2.

Table 1. Average Particle Size Values for Alumina Suspensions, pH 8.0, 25°C

Sample	Average Particle Size (nm) $\pm 2\%$	Average Particle Size (nm)* $\pm 2\%$
Al_2O_3	2030	740
$Al_2O_3 + CG$	790	720

*Suspension submitted to ultrasound effect during 5 min.

The data in Table 1 show that the addition of CG prevented the flocculation of alumina through the formation of a physical barrier that hinders the approximation of the particles, since the average particle size was considerably smaller in the presence of the polymer. It is observed that the suspension containing the polymer, presented little variation of particle size, when it is submitted to ultrasound effect. This result shows that in this pH, CG adsorption on the particle involves strong interactions. For the suspension containing only alumina, the decrease in particle size was significant, since the ultrasound supplies enough energy to overcome the interactions between particles, and therefore, they are kept further apart, preventing the action of the van der Waals attractive forces.

It is pointed out that the application of this technique, complimentary to viscosimetry, was essential for the evaluation of the effect of the addition of the polyelectrolyte. For example, around pH 8.0 (Figs. 4 and 5), the suspension with CG did not present any drastic change of viscosity in comparison with the alumina suspension. However, the values in Table 1 show that the particles are considerably less aggregated when CG is present.

To evaluate the stability of the suspensions as a function of time, photon correlation spectroscopy study was carried out. The effective diameter of the particle was measured as a function of time for several pH values. It must be pointed out that the effective diameter values over 2,000 nm must be considered only as indicative of particle size increase, since the highest accurate measurement limit of the apparatus used is 2,000 nm.

It can be noticed that when cosmedia guar is present, the particle size increases as a function of time, similarly as when there is only alumina (Fig. 6). Apparently, after some time, there occurs aggregate dissociation in the presence of CG. However, the particles do not shrink back to their original size. Even tough larger particle sizes are observed (in comparison with t = 0), the suspension containing cosmedia guar keeps the particles dispersed for a longer timer (around 2 hr), in comparison to the suspension containing only alumina, which sediments after the first initial minutes.
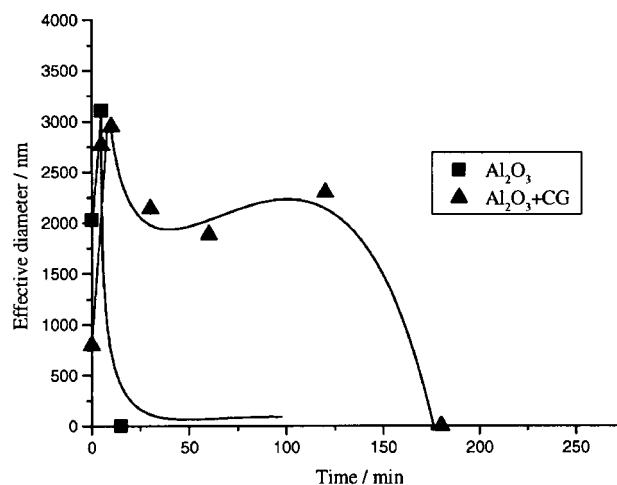
Figure 6. Particle size as a function of time for aqueous suspensions of alumina and alumina/CG, pH 8.5, 25°C, without ultrasound effect. The points on the x axis indicate the time interval in which flocculation occurs.

Figure 7 shows the particle size variation, as a function of time, for the suspensions containing alumina and alumina/CG, submitted to ultrasound effect during 5 min. The comparison of these curves with those in Fig. 6, reveals that the ultrasound causes a decrease in the particle size. This treatment breaks part of the agglomerates, making the particles smaller and consequently, they will take longer to sediment, which allows them to stay longer in suspension. As mentioned, pH 8 was chosen because it is near
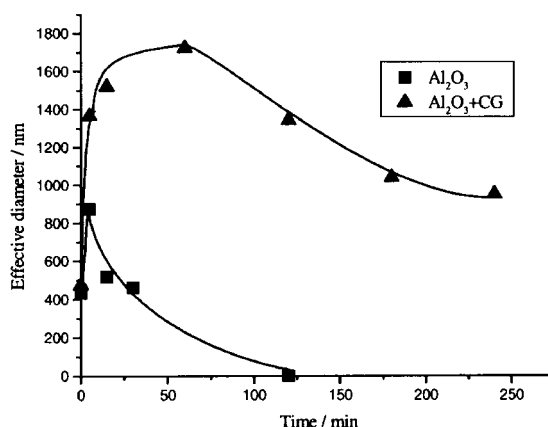

Figure 7. Particle size as a function of time for aqueous suspensions of alumina and of alumina/CG, 5 min of ultrasound, pH 8.5, 25°C. The points on the x axis indicate the time interval in which flocculation occurs.
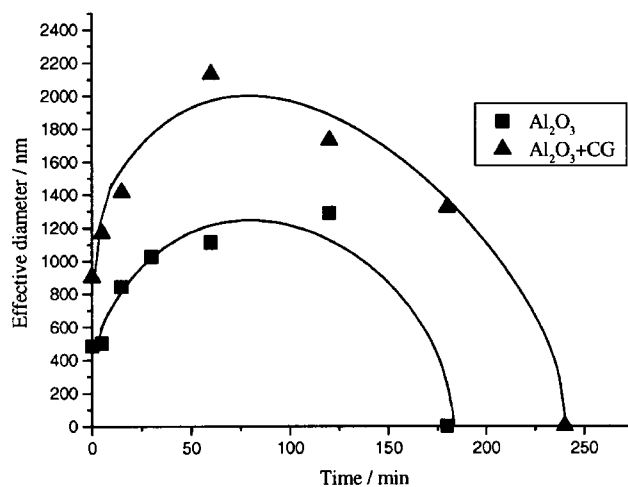
Figure 8. Particle size as a function of time for aqueous suspensions of alumina and of alumina/CG, 5 min of ultrasound, pH 5.6, 25°C. The points on the *x* axis indicate the time interval in which flocculation occurs.

the pH_{pzc} of the alumina used in the present work, that is, the objective was to verify the effect of the addition of CG in the less favorable condition.

Figure 8 presents the behavior of the suspensions of alumina and alumina/CG with 5 min under ultrasound effect, at pH 5.6. The comparison of Figs. 7 and 8 reveal that in an acidic medium the alumina/CG suspension presents larger values of particle size than those at the alkaline region pH (Fig. 7). In an acidic medium, alumina presents sites predominantly positively charged, which causes repulsive interactions with the positive charge of cosmedia guar. Hydrogen bonds are practically the only attractive interactions which can take place under these conditions. It must be pointed out that the viscosity is low at this pH (Fig. 5), but in that case, the measurements are made under stirring, which probably contributes to the different behavior observed, when the measurements of viscosity are compared with those of particle size.

From the comparison of Figs. 8 and 5, it can be concluded that near pH 6, viscosity also starts to increase, indicating that there may be particle agglomeration occurring.

Figure 9 shows the variation of particle size as a function of pH for both suspensions, alumina and alumina/CG, considering measurements made at t = 0. It can be noticed that when the polyelectrolyte is present in an acidic medium, the particle size is larger, which confirms that the adsorption of this macromolecule in alumina is not favored under this condition. For both suspensions, the pH in which the particle size increases corresponds to high values of viscosity (Fig. 5).
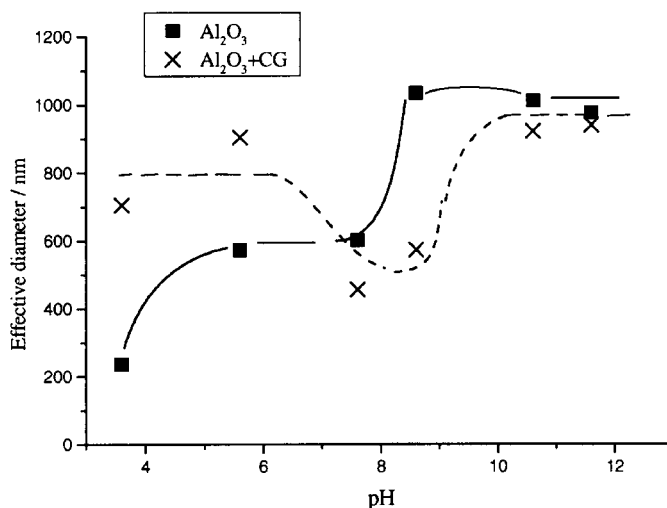
Figure 9. Particle size as a function of pH for aqueous suspension of pH of alumina and alumina/CG, 25°C.

CONCLUSION

The study of the behavior of the aqueous suspension of alumina in the presence of a cationic polyelectrolyte was evaluated by different techniques. The results obtained show that, if the viscosity measurements were considered in isolation, it could be concluded that cosmedia guar would not have a good performance as a deflocculation agent, because it does not lead to viscosity values much lower than those observed previously to its addition. However, with the measurements of particle size as a function of time, it can be concluded that the addition of this macromolecule keeps the particles dispersed for a longer time, in comparison with the suspension containing only alumina, mainly in alkaline medium.

Nevertheless, it must be pointed out that the CG used in the present work is not as effective as other dispersants usually used for alumina suspensions, as for instance sodium polyacrylates. Probably a CG with lower molecular weight than that used could lead to a better performance of this macromolecule as a stabilizing agent of aqueous alumina suspension.

ACKNOWLEDGMENTS

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