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Influence of the acid–basic character of oxide surfaces in dispersants effectiveness

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Abstract

Physical–chemical surface character has been described as a determinant factor in adsorbing polyelectrolytes onto oxide surfaces. Since basically composed by hydroxyl groups, the acidity or basicity induced by the bulk lattice in such groups seems to be of great relevance in the adsorption process. The influence of such properties in the adsorption of polyacrylic acid derivated polymers onto SnO_2 and Al_2O_3 surfaces is, therefore, studied in this paper. Polyacrylate acid molecules are observed to hardly adsorb onto the SnO_2 surface but strongly adsorb, as reported previously, onto the alumina surface. This behavior is explained based on the pronounced difference in relation to the acidity of both surfaces and, in this sphere of thought, a basic polymer (Chitosan; CS) is discussed as a functional dispersant for powders with acid surface character, such as SnO_2. Zeta potential measurements showed that this polymer raises the SnO_2 potential to +30 mV without pH variations.

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1. Introduction

One of the most challenging problems in the study of colloidal systems is obtaining the desired stability and rheologic properties of a suspension. One usually makes use of dispersing agents to achieve these properties that are of prime consideration in colloidal processing and are commonly regarded as the most important parameters to produce high-quality, high-performance, and reliable ceramic products [1]. The selection of an appropriate dispersant to optimize such properties is essentially dependent upon solvent characteristics, conformation process, and especially upon physical–chemical characteristics of the ceramic powder and surface [2].

Despite the focus of many studies, the influence of the surface properties in the dispersant effectiveness is not completely clarified, but one knows that surface chemical nature and impurities should play an important role in the adsorption of polyelectrolytes and, therefore, in their effectiveness as dispersants. The chemical nature includes the electron density of the surface chemical groups (essentially hydroxyls for oxides) as well as the relative quantity of such groups. Therefore, a modification of the surface, such as changes in the number of hydroxyl groups and the presence of adsorbed surfactants, changes the isoelectric point (IEP), the surface charging behavior and, therefore, its macroscopic properties, as the adsorption isotherms of dispersants [3,4].

The electron density related to the acidity of the surface chemical groups is not frequently treated as a determinant factor in the effectiveness of dispersants. However, similarly to the acidity of organic compounds that play fundamental roles in common reactions, special attention should be paid to it. The acidity of powders depends on its composition and on its crystalline structure. In fact, the surface of a powder is a mixture of many hydroxyl groups with different equilibrium constants. However, in dealing with macro-properties, a mean value is usually successfully applied and is actually the measured one in titration experiments.

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The acidity of chemical surface groups can be indirectly studied by observing the zeta potential, ζ, of the powder in suspension. Such potential represents the electrical potential evaluated in the shearing plan when a particle is moving under influence of an electric field [5–8]. The value of such potential can, therefore, be used as a reference of the surface charging behavior and reaction with the surrounding components of the medium, including solvent molecules, polyelectrolytes in solution, and potential determining ions, indicating a relative acidity of the surface and helping to understand the physical–chemical behavior.

The target of this work is to relate this relative acidity to the effectiveness of dispersants in different oxides. The dispersants based on polymers derived from acrylic acids are the most common when dealing with aqueous suspensions of ceramic oxides. These dispersants are expected to bind the surface possibly through hydrogen bonds, electrostatic attraction, and/or covalent bonds, and increase the repulsive potential between the particles [9]. The effectiveness of ammonium polyacrylate in dispersing concentrated alumina suspensions has been extensively proved [10,11], however, the addition of these polymers during electrophoretic deposition (EPD) of SnO_2 suspensions decreases the rate of deposition [12]. Moreover, an increase in the viscosity and a decrease in the zeta potential are observed when high-dispersant concentrations are added. These results suggest that this dispersant is not suitable for this particular system.

SnO_2 or Al_2O_3 are not soluble in either basic or acid media, but their IEP fundamentally differ, being acid for SnO_2 (IEP = 4) and basic for Al_2O_3 (IEP = 9) [13,14]. Suggesting that the dispersant effectiveness is, in such case, determined by the adsorbing of the polyelectrolytes on the surface, we carefully study the charging behavior of the aqueous suspensions of both powders to clarify the differences in the surface of the powders that influence the polyelectrolytes adsorption. Influenced by the results and proposed relations, the adsorption and dispersing effect of Chitosan (CS) is discussed. This polysaccharide is a derivative of chitin, which occurs in animals, particularly in crustaceans [15]. Chitosan is produced by alkaline deacetylation of chitin and is poly[*b*-(1→4)-2-amino-2-deoxy-D-glucopyranose], showing a lower dissociation constant than that of polyacrylate molecules.

2. Materials and methods

Tin dioxide (99.9%, Minasolo, Brazil, surface area = $7\,m^2/g$) and alumina (ALCOA A1000SG, Brazil, surface area = $10\,m^2/g$) powders were used as received. The solvent was deionized water. The analyzed dispersants were: Duramax D-3005 (ammonium polyelectrolyte salt), Duramax D-3007 (ammonium salt based on an acrylic copolymer), Duramax D-3021 (ammonium polyelectrolyte salt), all provided by Rohm and Haas; and Chitosan with molar mass 150,000 g/mol, provided by Fluka (99%, Switzerland). The main information of the acrylic dispersants are shown in Table 1.

Table 1
The added dispersants and their main features

Name	Concentration (wt.%)	Mw	Counter-ion	pH
D-3005	35	2400	NH_4^+	7.2
D-3007	45	5000	Na^+	3.2
D-3021	40	2500	NH_4^+	7.2

Source: Rohm and Haas.

SnO_2 aqueous suspension (2 vol.%) was prepared with no dispersant to evaluate the pH influence on the zeta potential measurements. From the initial value (~4), the pH of the suspension was raised to 13 by adding a 2N KOH (Nuclear, Brazil) solution. Acid titration was carried out by adding a 2N HNO_3 (Nuclear) solution. The same method was applied to an aqueous 5 vol.% alumina suspension, with initial pH equal 9.

SnO_2 aqueous suspensions (2 vol.%) were prepared to study the influence of each polyacrylate dispersant on the surface potential variation. The polymer concentration in the suspension was systematically increased by adding a 1:5 aqueous solution of each dispersant.

To evaluate the activity of CS as a dispersant in SnO_2 suspensions, the zeta potential of 1 vol.% suspension was measured during the addition of a 1 g/l solution of CS, acetic acid 0.1 M (Nuclear).

The electrokinetics sonic amplitude (ESA) method, which is able to determine the zeta potential of ceramic suspension and the electrophoretic mobility of these systems, was used to study the previously described experiments. This technique is based on the electroacoustic effect induced by the application of a high-frequency electric field between two electrodes within the ceramic suspension. The field-induced force deforms the electrostatic charge distribution of the particle and an alternate relative movement between the particle and its double layer appears. This movement generates a mechanical wave with the same frequency of the applied field and the equipment detects this signal [5,16].

The amplitude of the sound wave generated is a function of the charges dislocated by each particle, the particle concentration and the applied field. The signal is detected by a piezoelectric sensor which releases an electric amplitude in proportion to the collected input. The equipment was a ESA MATEC 8000, which can simultaneously record the temperature, ionic conductivity, pH, and zeta potential of the suspension.

3. Results

For a better comprehension of the interaction between the surface of SnO_2 and Al_2O_3 with polyelectrolytes, we initially studied the behavior of both surfaces in aqueous suspensions and the influence of the pH in the surface

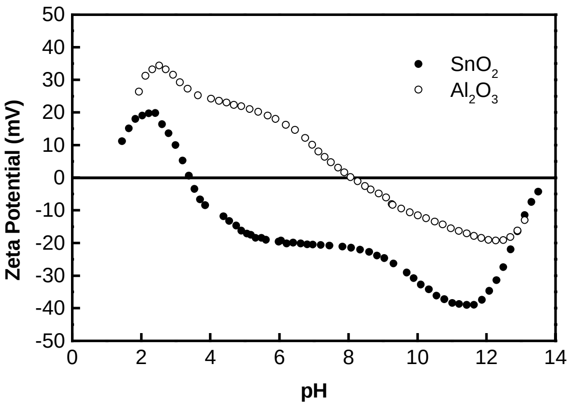

Fig. 1. Zeta potential variation of SnO_2 (2 vol.%) and Al_2O_3 (5 vol.%) suspensions as a function of pH.

charging and chemistry. In Fig. 1, the titration of both SnO_2 and Al_2O_3 aqueous suspensions shows the isoelectric points of the SnO_2 and Al_2O_3 suspensions near 3.5 and 8, respectively, being close to those described in the literature [14]. These values suggest a basic character for the alumina surface and an acid character for the tin oxide surface in relation to the water. Similar acid/basic character is readily observed when the powders are directly dropped in water. For SnO_2, the pH falls to values around 4, while for alumina it raises up to about 9. Such behaviors can be summarized by the familiar surface charging equations as follows:

$$M - OH + OH^- \Leftrightarrow M - O^- + H_2O \quad (1)$$

$$M - OH + H^+ \Leftrightarrow M - OH_2{}^+ \quad (2)$$

However, an interesting point may be noted in both titration curves, showing the surfaces to work a little more complicated and the above equations not to describe the reactions completely. There are two maximum zeta potential values (in modulus) in each plot in Fig. 1. Note that higher ζ potential values (in modulus) are observed at pH opposite to the IEP of the respective oxide, i.e. for the SnO_2 (IEP $=$ 3.5), the maximum potential obtained was -39 mV at pH 11.5, and for alumina ($pH_{IEP} = 8$), the maximum value was $+34$ mV at pH 2.4. These results confirm the tendency of the basic character oxide surface to highly interact with H^+ ions, and of the acid oxide surface to highly interact with OH^- ions. Actually, the basic side of the titration graph of the alumina suspension shows an inflection point at about pH 8. This behavior could be explained proposing the existence of one simple kind of interaction between the surface and the OH^- ions of the surroundings (Eq. (2)). In the acid titration, however, one more inflection is observed. Similarly, the titration of the SnO_2 suspension shows two inflection points at pH 9 and 3.5. These additional inflections, that could not be explained by the equations above, may arise from the presence of two or more different surfaces, e.g. for SnO_2, (1 1 0) and (1 0 1) planes may be present in the surface, and therefore two different ion adsorption constants would appear [17].

Another reasonable explanation for this behavior arises from the dissolution of the oxides. Several oxides are usually described as “insoluble” whereas, in fact, they are soluble but dissolve very slowly. As a semiconducting oxide, SnO_2 should follow the dissolution process: charge transfer to surface; ion formation (Sn^{4+} and O^{2-}); Sn^{4+} transfer to solution; H^+ transfer to O^{2-}, and OH^- (or H_2O) transfer to solution [10]. This process obviously changes the surface charge density and may be promoted at alkaline pH, generating the inflection in the SnO_2 titration graph.

Alumina should work similarly, showing more than one plane on the surface and/or little solubility during titration but, despite such complicating parameter involving both surfaces, the acid character of SnO_2 and the basic character of Al_2O_2 are by far the preponderant factor when dealing with adsorption reactions and, for simplicity and without lost of generality, just one surface will be treated in the discussion of the observed adsorption behaviors below.

3.1. Polyacrylates and SnO_2

Fig. 2 shows the influence of each polyacrylate dispersant on the zeta potential and on the pH of a SnO_2 suspension. The zeta potential of the SnO_2 particles decreases with increasing concentration of all the dispersants studied. The maximum potential obtained was about -23 mV with the D-3021 dispersant.

Note that both D-3005 and D-3021 molecules were kept in alkaline suspensions (in relation to the polymer ionization pK_a), therefore, the dissociation of their acrylate groups gives rise to negative charges. Therefore, a possible but erroneous explanation for the high-potentials obtained may come from the polymers adsorption. When the polymer is adsorbed on the oxide surface the negative charges may contribute to increase the zeta potential and the stability of the suspension. However, both D-3005 and D-3021 led to a very sensible change in the suspension pH, which reaches a final value of about 7.5. On the other hand, the D-3007 dispersant does not alter the pH of the suspension, which is maintained around 3.5.

Since the acrylic polyacids-derived dispersants, such as D-3005 and D-3021, must remain ionized to be soluble in aqueous solutions, D-3005 and D-3021 solutions have pH 7.2, and D-3007 solution pH 3.2 (Table 1). Therefore, the pH variations detected in the experiments are due to the pH difference between each dispersant solution and the initial system. Since the initial pH of the SnO_2 suspension is equal to 4, the pH values after the addition of D-3005 and D-3021 are expected to increase; on the other hand, lower pH values are expected after the addition of D-3007. As it can be seen in Fig. 1, these pH variations highly influence the surface charges.

Fig. 3 shows the variation of ζ as a function of the pH of the suspension with increasing dispersant concentration. The figure demonstrates that the potential variation with the addition of D-3007 is not accompanied by a pH variation as

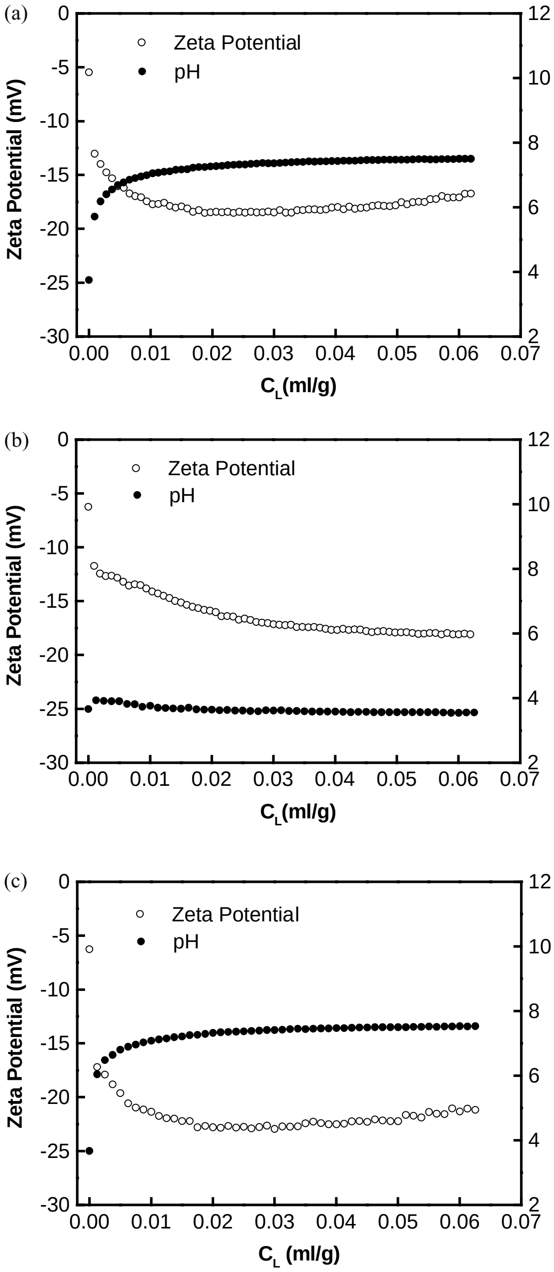

Fig. 2. Zeta potential and pH of a SnO_2 suspension (2 vol.%) as a function of dispersant concentration (per gram of SnO_2). Dispersants: (A) D-3005; (B) D-3007; and (C) D-3021.

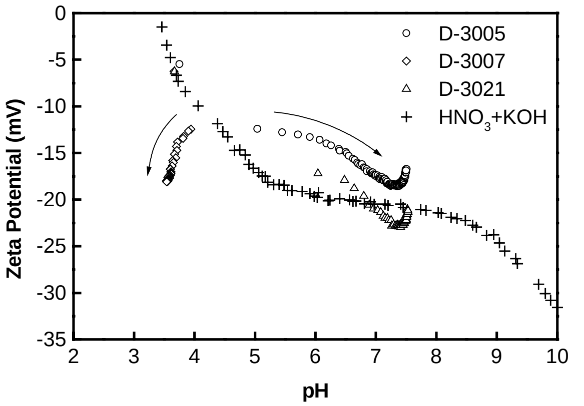

Fig. 3. Zeta potential as a function of the pH for SnO_2 suspensions with increasing dispersant (D-3005, D-3007, and D-3021) concentration (per gram of SnO_2) and titrated with HNO_3 and KOH.

it is observed for the others dispersants. The variation of the zeta potential with D-3005 and D-3021 approaches that with the addition of KOH and HNO_3. But the most important remark in Fig. 3 is that, for D-3005 and D-3021, the zeta potential reaches its maximum value when the pH is equal to the final pH of each dispersant solution. This means that the ζ variation may be directly related to the pH variations rather than to the polymer adsorption.

This behavior explains the phenomenon observed during EPD of SnO_2 with ammonium polyacrylate-based dispersants [12]. The decrease in the deposited mass occurs due to the increase in the suspension viscosity. Since this additive does not adsorb on the SnO_2 surface, the long polymeric chains is responsible for making the system more viscous. Hence, the mass deposition rate would decrease, as proposed by the described model.

No significant changes in the pH are observed in the D-3007 experiments and the surface potential increased significantly. However, the values of potential obtained in this experiments were under −19 mV and a relative unstable suspension still results. This may indicate that there is certainly the adsorption of the polymer, but this adsorption must be decreased by the surface intrinsic charge. That is, SnO_2 particles are negative in aqueous suspensions with the addition of no additives. This charge may repel the negative charged polymer and avoid, or minimize, adsorption.

3.2. Polyacrylates and Al_2O_3

Fig. 4 shows the pH and zeta potential variation of Al_2O_3 suspensions during the addition of the polyacrylate dispersant solutions. Since there are no considerable pH variations, and the zeta potential reaches values higher than −20 mV, D-3005 and D-3021 seems to be the responsible for the effective stabilization of the system. D-3007, however, clearly changes the pH of the suspension towards acid values. In addition, the ζ values are considerably smaller than the achieved by D-3005 and D-3021 (Fig. 4).

Fig. 5 shows the variations of the zeta potential as a function of the pH with increasing dispersant concentration. It is clear that the addition of the D-3005 and D-3021 does not change the pH of the suspension, however, D-3007 does, changing, therefore, the surface potential. Nevertheless, this fact is not a sufficient argument to ignore D-3007 adsorption. That is, since the potential variation does not follow the observed behavior in Fig. 1, where only the pH charging is present, the dispersant seems to adsorb onto the alumina surface and change the double layer structure, increasing negative electric charges. However, the decrease

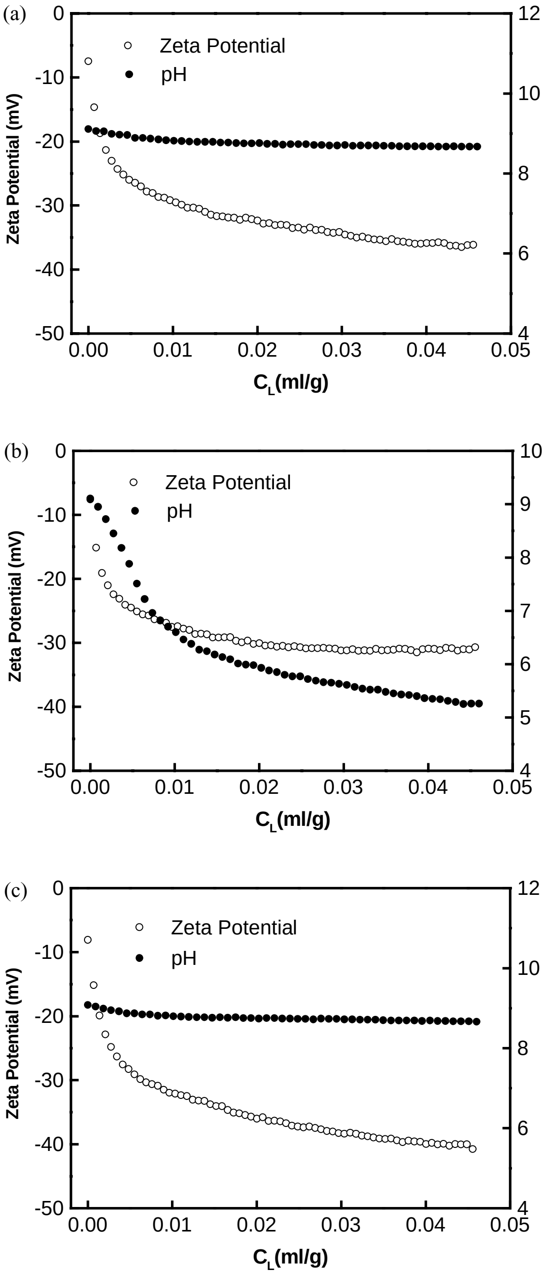

Fig. 4. Zeta potential and pH of a Al_2O_2 suspension (5 vol.%) as a function of dispersant concentration (per gram of Al_2O_3). Dispersants: (A) D-3005; (B) D-3007; and (C) D-3021.

in the pH forces the zeta potential to be smaller than the values obtained with D-3005 and D-3021.

4. Discussion

The addition of the D-3005 and D-3021 solutions to the SnO_2 suspensions seems to modify the zeta potential by increasing its pH. In the case of the alumina, this effect may be associated with the adsorption of polymeric chains to the alumina surface by hydrogen bonds [2]. As mentioned in Fig. 1, there is a great affinity between the SnO_2 surface and OH^- groups. On the other hand, the Al_2O_3 surface particularly interacts with H^+ groups due to basic characteristics. The addition of a polymer solution with basic pH to a SnO_2 suspension may, therefore, generate a competition for adsorption between the OH^- groups and the polymers. The OH^- interactions are certainly stronger since these ions are potential determining ions. Hence, this interaction would occur more easily than the hydrogen bonds formation between the oxide surface and the polymeric chains. In addition, the negative charges generated by the dissociation of adsorbed hydroxyl groups will prevent the polymer adsorption by electrostatic repulsion.

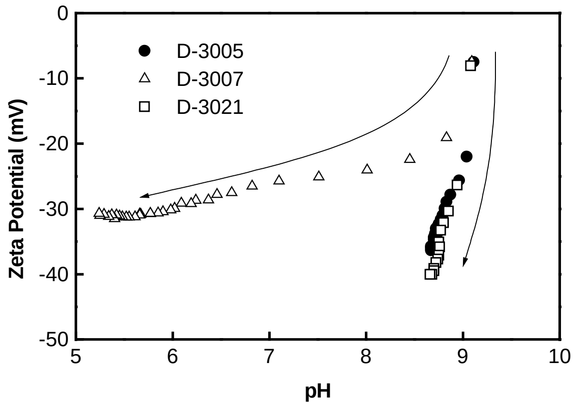

Fig. 5. Zeta potential as a function of the pH for Al_2O_3 suspensions with increasing dispersant (D-3005, D-3007, and D-3021) concentration (per gram of Al_2O_3).

In the case of the alumina suspensions, the initial pH is higher than that of the dispersant solutions. Therefore, the polymeric molecules can adsorb to the surface by hydrogen bonds since there is no competition for adsorption with hydroxyl surrounding ions.

When an acrylic dispersant solution, such as D-3007, is added to the alumina suspension, there is a competition for adsorption between H^+ ions and negatively charged polymers since the pH of the dispersant solution is lower than the one initially dispersed. Since the proton (determining potential ion) preferentially adsorbs to the surface, the zeta potential decreases and its maximum value is considerably lower than the ones reached with the addition of the other dispersants.

The presence of hydroxyl groups onto the surface of oxide powders is actually a determining factor for the adsorption of dispersants. However, the experiments showed that the same dispersant is effective or not depending on the oxide. This is related to the acid–basic character of the surface, which is determined by the oxide metal, e.g. Al or Sn. This character, associated with the molecule acidity, will determine the adsorption and effectiveness of the dispersants; i.e. when basic dispersant solutions are introduced in acid oxide suspensions, the competition with hydroxyl groups will avoid the polymer adsorption and vice versa. It is obvious

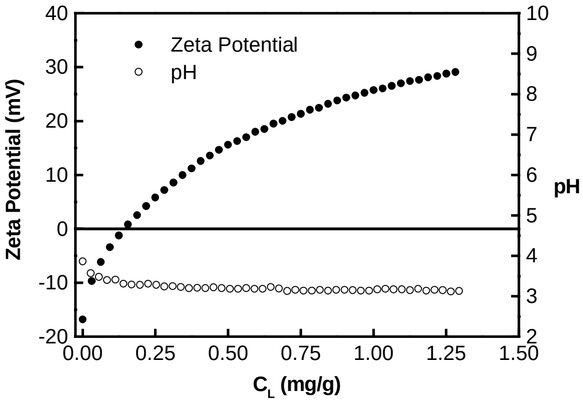

Fig. 6. Zeta potential variation of SnO_2 (1 vol.%) as a function of Chitosan concentration (per gram of SnO_2, C_L).

that changing the pH of the dispersant solution to a value equal to the suspension one does not solve the problem, since at different pH, the molecules could not be charged, and even if it is soluble in such condition, there would be no electrostatic stabilization. Note that the explanation given above is not true only for Sn and Al oxides. It depends mostly on the acidity of the powder, which can be determined by its IEP.

According to the results observed above, we may expect that a polymer, whose solution pH is close to the SnO_2 suspension, would preferentially absorb onto the surface since no potential determining ion excess would be present. Moreover, the polymer must have a molecular structure capable of forming hydrogen bonds with the surface and with chemical groups with opposite charges to the surface. These conditions were observed in choosing the polymer CS as the dispersant [18].

Fig. 6 shows the zeta potential variation of a SnO_2 suspension with increasing CS concentration. Note that the potential reaches +30 mV at about 1.3 mg of CS per gram of SnO_2. The pH of the system is maintained constant at about 4; and therefore the potential increasing can certainly be attributed to the adsorbed polymer charges. The formation of hydrogen bonds between the surface hydroxyl groups and the CS ones was supposed.

5. Conclusions

The adsorption of polymers onto the surface of a ceramic oxide depends on the type of polymer and on the acid/basic surface character. In basic IEP oxide suspensions, such as alumina, acid polymer adsorption occurs in basic medium, probably through hydrogen bond formation, and an increase in the zeta potential is observed and attributed to the ionized dispersant electrostatic charges. In acid IEP oxide suspensions, such as tin dioxide, there is a competition for adsorption onto the surface between the surrounding hydroxyl groups and the acid polymer in basic media. Since OH^- is a potential determining ion, its adsorption occurs instead of the polymer adsorption. The negative electrostatic charges generated on the surface by OH^- adsorption prevent the negatively charged polymer adsorption from occurring by electrostatic repulsion. Therefore, the zeta potential fluctuations are attributed only to pH variations. This phenomenon is also observed in the results collected from the interactions between the alumina suspension and the D-3007 dispersant. In this case, there is a competition for adsorption between the polymer chains and the surrounding H^+ ions.

The main two questions that must be asked when choosing a dispersant for a specific oxide are, therefore: at which pH is the polymer charged (its pK_a) and is there any active binding site onto its structure at this pH? When the powder has a basic character the polymer must present charges at basic pH and vice versa. This avoids potential determining ion competition. If we restrict the binding problem to the formation of hydrogen bonds, the polymer must have non-dissociated hydroxyl groups on its structure. Moreover, it is preferable for the dispersant to have opposite charges to the surface.

These conditional points, when applied to SnO_2 suspensions, are satisfied by the polysaccharide Chitosan. This polymer shows positive charges at pH near 4 and hydroxyl groups ready to form hydrogen bonds. As expected, the zeta potential of a SnO_2 suspension reaches +30 mV in increasing CS concentration.

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