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The influence of the Chitosan adsorption on the stability of SnO_2 suspensions

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Abstract

The influence of the polyssacharide CS on the zeta potential variation of a SnO_2 aqueous suspension has been systematically studied. The maximum potential obtained for the suspension was about 30 mV, which is high enough to stabilize the suspension. No significant effects on the zeta potential variation were identified when the molecular weight of CS was raised. Kinetics experiments have also been carried out and the potential of the suspension was stabilized about 10 s after the addition of the polymer. A new procedure was proposed for obtaining the adsorption isotherm curve, studying its relation with ζ potential variation in increasing CS concentration. The method avoids some inconveniences of experimental procedures and the results obtained were very reasonable. The interaction of the CS with the surface was studied by FTIR and indicates that the most probable interaction is the formation of hydrogen bonds between the polymer and the surface hydroxyl groups. A deflocculating curve of a suspension of SnO_2 as a function of CS concentration is also presented, indicating that at about 1.5 mg of CS/g of SnO_2 the viscosity falls to zero.

Keywords: Chitosan; Dispersion; FTIR; SnO_2; Suspensions

1. Introduction

Tin oxide is an important base material for a great variety of gas sensors. The SnO_2 is a n-type semiconductor, with a 3.6 eV gap, and rutile crystal structure. The most stable surface of this crystal is related to the plane (110) and hence a polycrystalline material may be treated as having almost all surface planes like this.[1,2] The real situation is that 60% of surface planes are (110), 20% are (111) and 20% are (100),[3] but in dealing with surface reactions in suspension and in order to simplify discussions it is treated as being just (110).

Studying (110) planes at the surface, one may note that, in order to minimize surface energy, the (110) crystal may not terminate with a repetitive unity, as Sn^{4+}, since it would generate moments perpendicular to the surface. In this way, a preferential ionic layer termination sequence [(1O) (2O + 2Sn) (1O)] (Fig. 1) that has no dipole but a quadrupole [(2−)(4+)(2−)] will exist. The external oxygen layer forms a bridge between tin adjacent ions in order to complete the sixth coordination of at least half the ions on the surface.[1]

In aqueous suspension, water molecules interact with surface charges and their hydroxyl groups attach to the five-fold coordinated tin atom.[4] To explain some experimental results such as the decreasing in the pH of a SnO_2 suspension and its slightly negative zeta potential (−9 mV),5 it is proposed that the proton from the dissociated water stays in the bulk of the solution as H_3O^+ despite attaching to the nearly bridging oxygen on the surface.

PMMA [poly(methyl methacrylate)] is an acid molecule, usually with carboxyl groups that are found deprotonated at pH beyond 7. This molecule is usually used as a dispersant for powders such as Al_2O_3 with basic surface. One may say that this molecule binds to the surface of oxides in the same way citric acid does, i.e. hydroxyl groups are substituted by carboxyl ions.[6] However, hydrogen bond formation is also a reasonable way of binding. When PMMA molecules are added to SnO_2 suspensions they do not adsorb to particle surface and so the stability of the system is not affected.[5] In such systems hydroxyl ions are added at the same time

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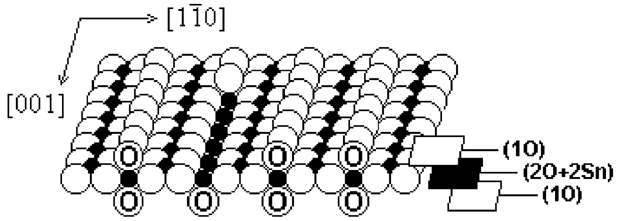

Fig. 1. Schematic representation of the SnO2 (110) surface. Small filled spheres are Sn cations, and open spheres are O anions. The surface Sn cations are 4 coordinate in the surface plane with further underlying O ion (visible in the second column) to give a total coordination number of 5, completed with the bridging O (after Jones et al.).[1].

as dispersant molecules, since the pH of the dispersant solution is significantly higher than that of the SnO_2 suspensions. These smaller and more mobile negative charged ions migrate to the surface faster than the PMMA macromolecules, generating negative surface charges, and repelling other PMMA molecules. This avoids hydrogen bond formation between the polymer and the hydroxyl surface.[5]

Dispersant molecules must follow some basic principles in order to be effective and generate stable suspensions: (1) molecules must exhibit an available anchor site at the pH in which they are going to be used; (2) they must also have a charge, especially opposed to the surface one, to facilitate the molecule transport stage of the adsorbing reaction. Finally, (3) the pH in which both sites are activated must be near the isoelectric point of the suspension to avoid the presence of undesirable ions, which could trouble the dispersant adsorption. The molecule chosen in this work was the Chitosan (CS, a polysaccharide).

Chitin is the second most important natural polysaccharide (cellulose being the first). It occurs in animals, particularly in crustaceans, molluscs and insects, where it is an important constituent of the exoskeleton, and in certain fungi where it is the principal fibrillar polymer in the cell wall.[7] Chitin is poly[b-(1→4)-2-acetamido-2-deoxy-D-glucopyranose]. The principal derivative of chitin is CS, produced by alkaline deacetylation of chitin. CS also occurs naturally in some fungi but its occurrence is much less widespread than chitin one. CS is poly[b-(1→4)-2-amino-2-deoxy-d-gluucopyranose].

The amino groups of CS are responsible for the basic character of the molecule, and are expected to be protonated at pH near 4, guaranteeing good solubility in water. The pK_a of CS, as commented above for polyeletrolytes, will depend on the charge density of the molecule as well as on the degree of n-acetylation for samples having the same fraction of neutralized $-NH^{3+}$ groups. The value of the pK_a for the monomer, d-glucosamine, has been reported to be 7.5,[8] but lower values were obtained for CS and were attributed to the strong electrostatic interaction between adjacent amino groups. Studies of specific viscosity of a solution of CS [0.36], i.e. with a degree of desacetylation of 36%, carried out by Park et al.,[9] suggest that the C (2)-$NHCOCH_3$ group becomes protonated below pH 3.5.

The degree of *N*-acetylation of CS is related to the low income of the desacetylation reaction. The CS used in this paper has a degree of *N*-acetylation of about 50% (CS [0.50]), hence nitrogened sites from CS as well as acetyl groups from chitin will be present in the polymer.

The intent of this paper is to check the possibility of utilizing CS molecules at low pH as a dispersant for SnO_2. Zeta potential, pH and electrical conductivity of SnO_2 suspension were measured during the addition of solutions of CS, in three different molar masses, using the ESA-8000 Matec equipment that makes it possible to measure the electro-acoustic signal (ESA, *Electrokinetic Sonic Amplitude*) simultaneously to pH, conductivity and temperature. The kinetics of adsorption for the molecules were studied and a study was also carried out of the rheologic behavior of a tin oxide suspension by adding CS.

A new way was also proposed for obtaining the adsorption isotherm curve, studying its relation with ζ potential variation in increasing CS concentration and, finally, the chemical interactions of CS with the surface of the oxide were investigated by FTIR spectroscopy. It was possible to determine the anchor sites involved in the fixation of the polymer to the surface.

2. Experimental procedure

A commercial tin oxide (Minasolo—99,9%), having specific area 7.3 $m^2 g^{-1}$ and a mean particle size of 0.06 μm, was employed. The solvent was deionized water. The chemical reagents CS with molar mass 150,000, 400,000 and 600,000 g/mol (Fluka 99%—Basel Sweden) were used as received. Acetic acid 0.1 M (Nuclear—Brazil) was also used in the tests.

Electrophoretic mobility of the particles used in this study was measured with a MATEC ESA-8000 measuring system; which uses ESA (*Electrokinetic Sonic Amplitude*) technique for the zeta potential calculation.[10,11] The rheometric measurements were carried out using a Brookfield DV-II+ viscosimetry equipment. The FTIR (Fourier transform infra red) experiments were carried in a Nicolet Magna-IR 560 spectrometer measuring system using diffuse reflectance, transmission or attenuated total reflection (ATR) techniques.

ζ Potential measurements of a 1-vol.% suspension were carried out during the addition of a 1 g/l solution of CS in HAc 0.1 M at 0.05 ml/30 s. First of all, the pHs of the SnO_2 suspension were adjusted to the value in which the surface potential is near zero (pzc). The conductivity of the suspension was also adjusted to the value presented by the CS solution, i.e., 650 μS/cm, and the pH of the CS solution was adjusted to the same pH of the suspension at zero surface charge (about 3.9). This procedure avoids the potential deviations due to pH changes, and therefore, all modification in ζ is related to the adsorption of the dispersant. Temperature was room temperature, 25 °C. The kinetic adsorption experiment of CS was carried out on the ESA equipment, rapidly adding 8.9 ml of a 3 g/l CS solution (pH and conductivity adjusted as mentioned above) to a 1-vol.% suspension of SnO_2. Time for ζ stabilization was then recorded. Temperature was 30 or 15 °C.

CS spectra were run as KBr disk after heating for 24 h at 70 °C. SnO_2 and SnO_2 with adsorbed CS were studied by using a diffuse reflectance accessory in which the surface of the powder is analyzed. The powders were also treated at 70 °C for 24 h to eliminate water molecules that could be adsorbed onto the surface. Adsorbed water molecules may mask O–H stretches since such molecules also have O–H vibration bands, which could overlay the studied ones. SnO_2 with adsorbed CS was obtained after the centrifugation (10,000 rpm) of a SnO_2 suspension 1-vol.% containing 2 mg of CS per gram of the oxide.

Suspension 5-vol.% of solid loading was prepared and the viscosity of the system was measured at 200 rpm, at systematic increments of CS, in order to study the rheometry of the system. Before each viscosity measurement suspensions were agitated for 15 min in order to homogenize the system.

3. Results and discussion

3.1. Zeta potential measurements

The zeta potential variation of particles in a 1-vol.% suspension of SnO_2 with the addition of CS solutions (1 g/l) is shown in Fig. 2.

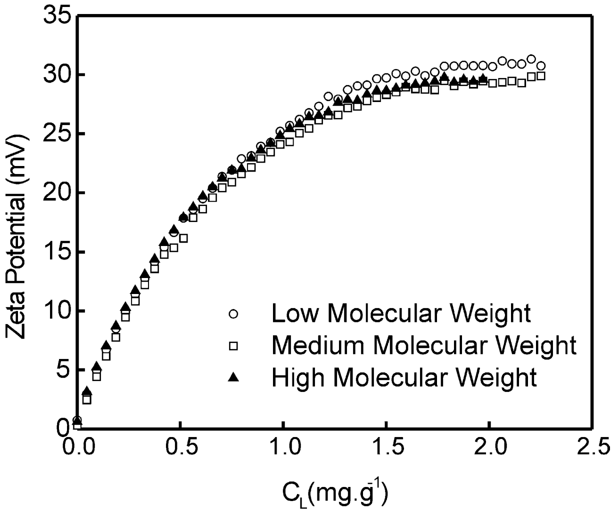

Fig. 2. Zeta potential variation of SnO_2 (1-vol.%) as a function of chitosan concentration (per gram of SnO_2, CL): Low molecular weight (○), medium molecular weight (×) and high molecular weight (●).

ζ Potential is raised to positive values in increasing CS concentration and reaches an upper limit of 30 mV at about 1.5 mg CS/g SnO_2. At this point the CS adsorption is supposed to have reached a maximum and the surface is saturated. Beyond this point an increase in CS concentration does not alter the potential and stays in the bulk of the solution. Conductivity and pH in these experiments were kept constant, and therefore surface charges may be attributed exclusively to CS adsorption.

Low molecular mass effect was observed in CS adsorption; the observed variations of the ζ potential were too low and may be attributed to equipment precision error.

Both CS and PMMA dispersants are supposed to bind surfaces through hydrogen bonds. Studies of SnO_2 systems with PMMA show that the adsorption is not satisfactory and this ineffective behavior is attributed to the competition of hydroxyl groups in adsorbing onto the surface. This happens since the pH of these dispersants is highly basic in relation to initial pH of the suspension (about 4), leading to an excess of OH^- ions in solution. The polymer charges will, therefore, repel surface negative charges (formed from OH^- adsorption) and adsorption will be decreased, because the distance from the molecule to the surface will not be enough for bond formation. Since there is no competition of OH^- groups (not present in this system) for the studied case of CS and, in addition, CS shows opposite charge to the surfaces, the approach is favorable and hydrogen bonds may easily be formed. Hence, CS adsorption is successful and produces a high charge generation, since the polymer charges are not involved in the linkage, but only in the approach of it.

A schematic model of the adsorption of molecules of CS to oxide surfaces is shown in Fig. 3.

Hydroxyl groups of the polymer participate in hydrogen bonds with the oxide surface. At the same time ammonium groups $-NH_3^+$ raise surface charges and hence ζ potential. However, we might state that the bonds may be formed between groups on the surface and acetyl groups of the monomer chitin. These π-bounded oxygens have an excess of electrons, which may interact with the surface forming hydrogen bonds in the same way as the alcohol groups. To study this situation we analyzed IR spectroscopy of the powder and the powder with adsorbed polymer (Section 3.3).

Fig. 4 shows the kinetic of adsorption of CS on the surface of the oxide at two temperatures, 15 and 30 °C. Note that the adsorption is extremely fast, about 10 s after the addition, and there is no significant temperature effect on it. It should be observed that the maximum potential obtained in these experiments was about 22 mV, i.e. considerably below the potential obtained in the first concentration experiment (Fig. 2).

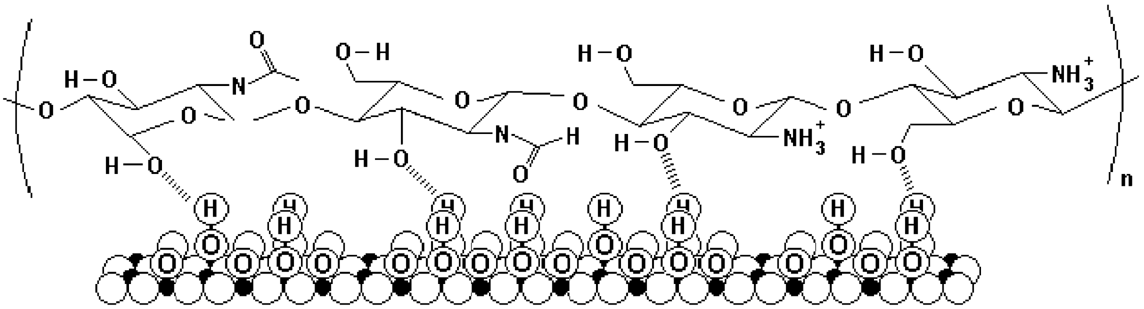

Fig. 3. Schematic representation of CS adsorption on tin oxide surface.

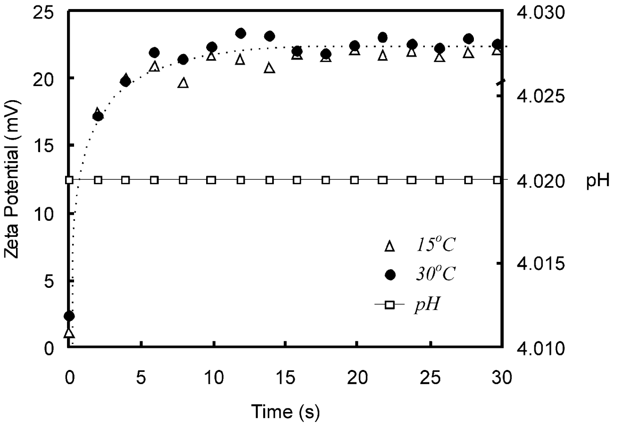

Fig. 4. Kinetic for the change of the zeta potential of SnO_2 when a rapid increment of a CS solution is done. Zeta potential is plotted against time at 15 °C (△) and 30 °C (●).

The explanation for it is given based on the structure of the polymer. In adding a high concentration of the dispersant to the suspension in a small period of time, one may say that the acquired configuration of the polymer at the surface is not the most stable one, and may call it a metastable conformation. This is due to the polymer anchor sites that bind to the surface in an unorganized way; this may hide some surface functional groups and decrease adsorption. Another explanation is more convincing and derives from the formation of hydrogen bonds among CS molecules. This is highly possible since there are hydroxyl groups present in the molecule that could interact among them despite interacting with the surface. This happens especially at high molecule concentrations, where the probability of a molecule-molecule interaction increases and therefore its adsorption is neglected. At low rates of injection the potential reaches a higher limit because, in this case, few molecules are present in the system, and therefore the probability of the molecules interacting with the surface is much higher than the interaction with each other. It is important to note here that we are not neglecting the molecule-molecule interaction in the first experiment. This effect is certainly present and may be one of the causes for the potential not to be higher than 30 mV.

3.2. Adsorption isotherm

The adsorption isotherm was obtained from the zeta potential results. At very low concentrations of CS in a suspension, one may note a linear behavior of the potential as a function of the concentration. This leads us to consider the adsorption of the polymer to be high enough in order to discharge CS bulk solution concentration, and therefore all CS molecules injected are being adsorbed and charging the surface. This happens since the probability of the molecule to interact with each other and hence stay in the bulk is much lower than that of interacting with the surface. Therefore, a simple linear equation for the first points may be obtained. This equation, when extrapolated to high concentrations, would simulate the surface zeta potential as a function of CS concentration if the molecule had no adsorption limit. But that is obviously not true, and a plateau is always obtained. One may say now, with some certainty, that the difference between that expected potential in a total adsorption situation and the observed results, would give the quantity of CS that would stay in the bulk and hence, indirectly, would quantify the adsorbed CS as a function of CS total solution concentration.

This approach may only be applied since the conditions of the experiments were well controlled: pH and conductivity did not change significantly in increasing CS concentration, and hence charge generation may be attributed only to polymer adsorption. Fig. 5 shows the first points of the zeta potential curve in Fig. 2.

Fig. 6 shows the adsorption isotherm itself which reaches a maximum adsorbing weight, at almost 0.1 g of CS per liter, of 0.09 mg CS/m^2 of SnO_2.

The standard procedure for obtaining adsorption isotherms generally follows these steps:[12–14] (1) preparation of the suspensions with different dispersant concentrations; (2) centrifugation or filtration of the suspensions to separate the adsorbed polymer from the one in the bulk of the solution; (3) supernatant concentration is determined by different techniques. What we note here is that this procedure may involve some experimental errors. The problem appears in the process of centrifugation of the suspensions. When dealing with

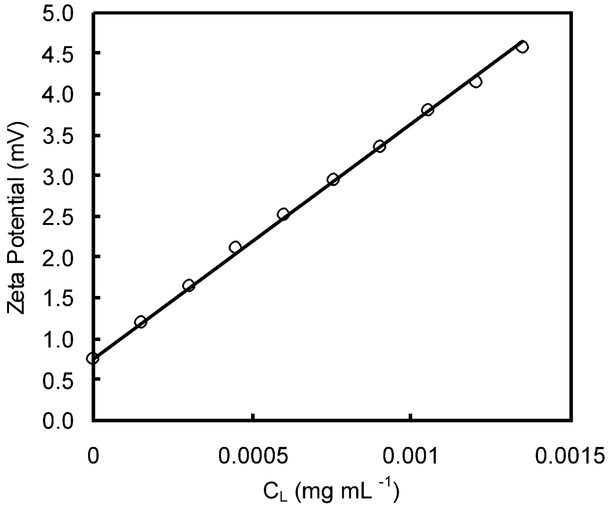

Fig. 5. First points of the zeta potential values plotted against CS concentration in the liquid (C_L).

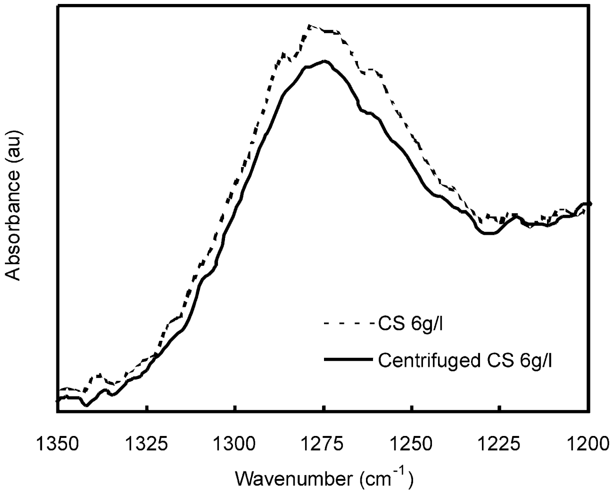

Fig. 7. ATR–FTIR spectra of chitosan solution at concentration 6 g/l (dotted line) and of the same solution after centrifugation (filled line).

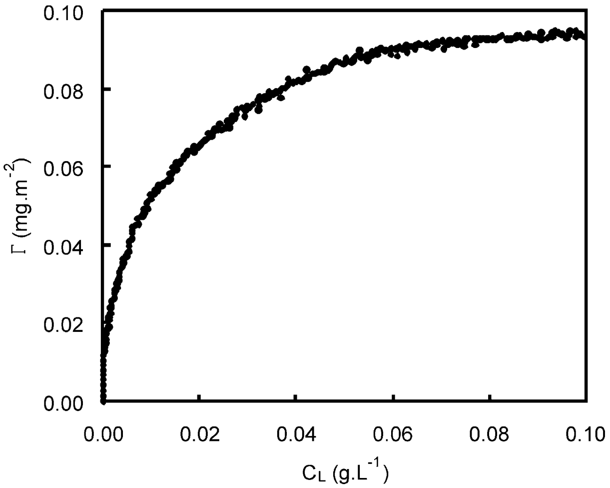

Fig. 6. Adsorption isotherm for CS with SnO_2. The polysaccharide concentration in the liquid (C_L) is plotted against the polysaccharide concentration on the solid surface (Γ).

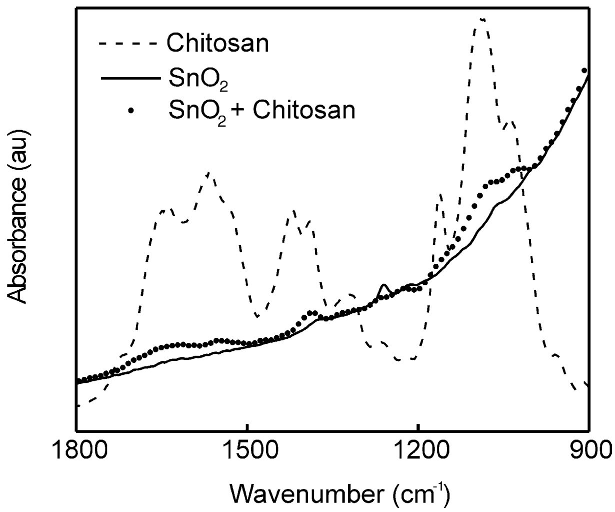

Fig. 8. FTIR spectra of pure chitosan, pure SnO_2 powder and of SnO_2 powder with adsorbed chitosan.

fine particles ($\sim 10^{-2}$ μm), the particle weight approaches that of the molecule, especially when dealing with polymers of high molecular weight. Hence, thermal movements acting on the particles and the molecules have the same strength. When centrifugation is carried out to overcome the thermal factor, both molecule and particle will precipitate at the same time. Therefore, the supernatant dispersant concentration will be artificially lower, and the isotherm will not match the real situation.

A simple experiment may show clearly that CS molecules, as SnO_2 particles, are easily centrifuged at 10,000 rpm (for 10 min.). Fig. 7 shows ATR–FTIR spectra obtained with two solutions of 6 g/l CS.

One of them was centrifuged as described. Note that there is a decreasing absorbency of the CS band at 1275 cm^{-1} after the centrifugation. Calculations of the area of both bands show that after the centrifugation the absorbancy band deacreases by about 7%. If the area can be directly related to the concentration, this means that the concentration of the centrifuged sample is near 5.58 g/l. Note that when we are dealing with extremely diluted solutions, this factor becomes very relevant.

Since the calculated isotherm presented here does not include a centrifugation step, the results presented are more believable and, furthermore, faster and more easily obtained.

3.3. IR spectroscopic analysis

IR spectra in Fig. 8 show absorbing bands for pure CS, pure $SnO_2$and SnO_2 with adsorbed CS (SnO_2 + CS).

IR spectra show decreasing absorbance in the O–H angular deforming bands of the hydroxyl groups of CS (1409 cm^{-1}) when it is adsorbed onto the surface. A decrease in some bands of the SnO_2 spectrum (1260, 1374, 3741, 3623 and 3478 cm^{-1}) can also be seen. The decreasing absorbency of CS band indicates the interaction of the polysaccharides hydroxyl groups with the surface. The most probable interaction is the formation of hydrogen bonds with surface hydroxyl groups and the removal of surface water molecules. A mechanism of interaction may also be proposed in which, as a first step, the polysaccharide would form hydrogen bonds with physisorbed water molecules, and in the second, step water molecules are displaced and hydroxyl groups on the oxide surface are involved in hydrogen bonding with the polysaccharide.[13]

The decreased 1260 and 1374 cm^{-1} bands of SnO_2 and the decreased axial deforming bands observed at 3741, 3623 and 3478 cm^{-1}, at first analysis, could be attributed to OH groups from the surface of the oxide. This explanation accords with the theory of hydrogen bond formation, and indicates that the surface hydroxyl groups may actually be treated as a weak acid, since similar hydroxyl vibrational bands can be found in the phenol IR spectrum (pK_a 9–11).[15] The SnO_2 cluster could, therefore, be attracting electrons from the oxygen atom, as the phenol ring does, and inducing a slight acid surface character.

It can also be seen here that the interaction of the polymer does not occur through hydrogen bonds involving acetyl groups (chitin monomer) of the polysaccharide. The C=O (~1640 cm^{-1}) stretching band present in the spectra of CS and maintained when it is adsorbed upon the surface shows that the interaction is not occurring.

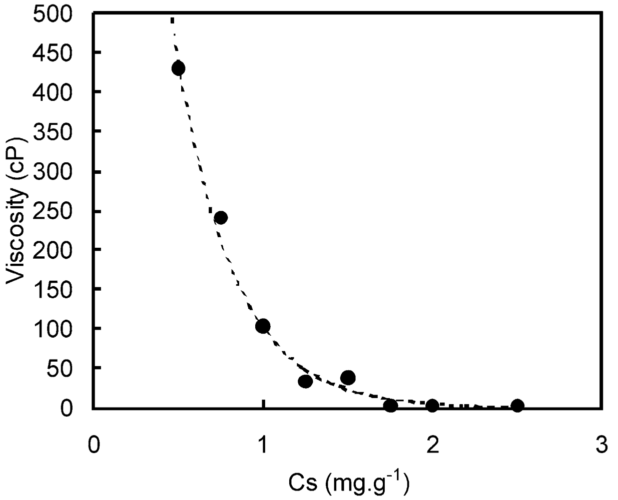

Fig. 9. Deflocculating isotherm at 200 rpm for a SnO_2 suspension with CS. The viscosity of the system is plotted against the polysaccharide concentration per gram of SnO_2 (Cs).

3.4. Rheometry of SnO_2 suspensions

A deflocculating curve of a suspension of SnO_2 as a function of CS concentration is shown in Fig. 9.

The curve shows exponential behavior and indicates that at about 1.5 mg of CS per gram of SnO_2 the viscosity falls to a minimum. At this concentration of CS, as indicated in Fig. 2, the potential is about 30 mV. Hence, CS is raising particle potential and enlarging particle repulsion forces, lowering the viscosity of the system. The data presented in Fig. 9 was obtained at an angular speed of 200 rpm, but for all speeds applied to the spindle, the system showed the same behavior. As the concentration for lowering viscosity follows the potential variation, it may be proposed that the interaction is predominantly electrostatic and small steric effects are observed.

4. Conclusions

The polysaccharide CS seems to be a good dispersant for SnO_2 aqueous suspensions. The maximum potential obtained for the suspension was about 30 mV after the addition of CS. Since the system showed no pH and no conductivity variation, the zeta potential increasing is proof of CS adsorption on the surface. Kinetics experiments showed that the adsorption is extremely fast, about 10 seconds after the addition, and there is no significant temperature effect on it. Although it was observed that the maximum potential obtained in the kinectics experiments were about 22 mV. The explanation for this behavior may come from the formation of hydrogen bonds between CS molecules in the bulk of the solution. It was also observed that changes in the molecular weight of CS alter neither the variation nor the maximum potential obtained for the suspension.

A new way was proposed for obtaining the adsorption isotherm curve, studying its relationship to ζ potential variation in increasing CS concentration. The method avoids some inconveniences of experimental procedures, and the results obtained were very reasonable. However, they should be compared with experimental data.

IR spectra indicate the interaction of the polysaccharides hydroxyl groups with the surface. The most probable interaction is the formation of hydrogen bonds with surface hydroxyl groups and the removal of surface water molecules. The bonds formation is also helped by electrostatic attraction between the surface and the molecules, which has opposite charges to the former.

A deflocculating curve of a suspension of SnO_2 as a function of CS concentration was presented, the curve shows exponential behavior, and indicates that at about 1.5 mg of CS per gram of SnO_2 the viscosity falls to a minimum. The effect of deffloculation comes from the electrostatic repulsion generated by adsorbed CS and probably by steric effects.

Acknowledgements

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