

EFFECT OF CMC AND PH ON THE RHEOLOGY OF SUSPENSIONS OF ISOTROPIC AND ANISOTROPIC MINERALS

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ABSTRACT

Rheological measurements have found a wide array of applications in mineral processing research. Rheological properties of mineral suspensions are highly dependent on the mineral surface properties as described by DLVO theory, and the relationship between these properties and inter-particle interactions is well established. In this paper, rheological properties of mineral suspensions are used to study the differences in behaviour of isotropic talc and anisotropic zirconia minerals as a function of varying properties of the suspension medium, such as pH and polymer dosage, specifically carboxymethyl cellulose (CMC).

It was found that the rheological tests when carried out in parallel with electrophoretic or point of zero charge measurements, clearly reveal differences between behaviour of the suspensions of isotropic and anisotropic minerals. These differences are further accentuated with the addition of carboxymethyl cellulose (CMC).

INTRODUCTION

Among various experimental techniques which are used in the mineral processing related research, rheological measurements are becoming quite common. Since efficiency of many processes directly depends on viscosity of the medium, (e.g. dense medium separation, wet grinding, etc.) such measurements can be used to improve these operations. Rheological measurements can be used to detect conformational changes in solutions of polymers that depend on polymer-solvent interaction. Such changes determine flocculation/stabilization phenomena in mineral suspensions. Rheological measurements can also be used to study particle-particle interactions since the rheology of dispersed systems is sensitive to aggregation/dispersion of particles in suspensions.

The inter-particle interactions in suspensions are largely dependent on factors such as suspension concentration, particle shape, particle size, and mineral surface properties as described by DLVO theory. According to the DLVO theory the particle-particle interactions result from the balance between attractive dispersion forces and repulsive electrical forces. This situation is simple for isotropic minerals (e.g. quartz) since electrical charges on different surfaces of such crystals are identical. However, it may be very complicated for anisotropic minerals. Talc belongs to this group of minerals. Among the experimental techniques that can be used to delineate such effects a very important position is occupied by rheological measurements [1].

The aim of this work is to compare the rheological behaviour of suspensions containing particles with different surface properties, specifically isotropic zirconia and anisotropic talc particles.

BACKGROUND

Rheology of mineral suspensions and particle surface properties

The relationship between the rheological behaviour of a concentrated suspension and inter-particle forces acting within that suspension is well established [2-5]. When used in conjunction with DLVO theory [6, 7], rheological measurements can provide useful information with regard to the nature of the particle surface charge, particle size and concentration within the suspension. The distribution of charge on the surface of the particle plays an important role in determining the rheological behaviour of a given suspension, and the rheological behaviour of isotropic particles can be distinctly different from that of anisotropic particles. Coagulation of the suspension of isotropic mineral is at its maximum around the iso-electric point of that mineral. This results in maximum yield stress values when measured against concentration of potential-determining ions (e.g. pH) [2]. The behaviour of the suspensions of anisotropic minerals in suspension is very different. Such

minerals do not have a single defined iso-electric point. Therefore, when the suspension yield stress is measured as a function of pH, the peak occurs at the point where the electrostatic attraction between the oppositely charged particle planes is at its maximum [8, 9].

The use of yield stress measurements as a function of solution pH in conjunction with electrophoretic and point of zero charge measurements can provide important information on the nature of the particle surface charge. Such techniques have been used to determine the surface charge characteristics of anisotropic kaolinite particles. They confirmed that the faces of kaolinite carry a negative charge which is independent of pH, while the electrical charge of the edges depends on pH [5, 8, 10, 11]. Similar work was performed on talc, another anisotropic mineral, and showed that its faces also carry a negative charge [9].

Effect of polymers on mineral suspensions

Long chain polymers are common reagents in the mineral processing industry. They are frequently used as flocculants in settling operations and as depressants in flotation. Carboxymethyl cellulose (CMC) is commonly used as a depressant to prevent hydrophobic gangue materials (e.g. talc) from entering the flotation froth. CMC's are anionic polymers and are known for their dispersant properties [12, 13]. The main dispersion mechanism of these polymers is electrostatic stabilisation, where negative polymer molecules contribute to the overall negative charge of the particles. An increase in the negative charge of the particles increases the repulsive electrostatic inter-particle forces, causing the suspension to disperse.

The efficacy of the dispersion is dependent on the degree of adsorption of the polymer molecules onto the mineral surface. The mechanisms of this adsorption have been widely studied. Since CMC's are anionic, the likelihood of electrostatic bonding being one of the adsorption mechanisms is high. However, several studies [14, 15] ruled out this possibility on the basis that the adsorption of CMC onto talc failed to reverse the zeta potential of mineral particles. The suggested bonding mechanisms were hydrogen and hydrophobic bonding. However, a recent study [16] showed a change in the apparent isoelectric point of talc suspensions as a function of CMC dosage and suggested a stronger presence of electrostatic forces in the mechanism of CMC adsorption. An acid/base interaction mechanism was also proposed [17], whereby polymer molecules interact chemically with metal hydroxide sites present on the mineral surface.

The adsorption of CMC was also found to be dependent on pH [14]. The adsorption isotherms of CMC onto talc exhibit a sharp increase in acidic pH, resulting in a decrease in the floatability of talc. A similar effect was noted for solution ionic strength [14, 18], where the adsorption isotherms increased dramatically with increasing ionic strengths of the suspension

medium. Both of these effects were attributed to the increased degree of coiling of CMC macromolecules, thus allowing for a denser adsorption; however this hypothesis has not been confirmed.

Polymers in solution

The degree of coiling of the polymer molecules has been shown to affect the adsorption density of these polymers onto a mineral surface [18]. The degree of coiling of polymers in solution can be inferred by measuring the viscosity of these solutions. When polymers are fully extended, the viscosity of the solution is generally high, due to the frictional forces between the long stranded polymers. However, once the molecules begin to coil, they start to act more and more like particles in a suspension, thereby decreasing the amount of intermolecular friction and thus decreasing the solution viscosity [19]. Intrinsic viscosity is a measure of solution viscosity that is independent of the concentration of polymer in solution [20], and therefore can be used to determine the degree of coiling of the polymer molecules in solution under varying conditions, such as change in ionic strength or pH of the suspension medium.

EXPERIMENTAL DETAILS

Materials

New York Talc is layered silicate mineral, well characterised as an anisotropic mineral [21]. Unlike other types of talc, New York talc has a clearly defined edge/plate crystal structure, which makes it a good model system to study anisotropic minerals. Talc is naturally floatable, and therefore polymeric depressants are commonly added to flotation systems to depress it out of the concentrate. For this reason, talc has been a subject of many studies pertaining to the adsorption mechanisms of CMC's [14-16, 18, 22]. New York Talc was obtained from Wards Minerals. The magnesium content determined by XRD analysis was 10.3 %. The talc was ground in a titanium ring mill to yield a p_{50} of 23 μm with the top size not exceeding 100 μm .

Zirconia is an isotropic mineral. Zirconia was chosen because its near spherical particle shape and well documented rheological properties [2, 3]. Zirconia was obtained from Richards Bay Minerals. The Zr^{+2} content, determined by XRD analysis, was 87%. The sample also contained circa 8 % silica. The sample was pre-ground to a size distribution of p_{50} 18 μm , with the top size not exceeding 100 μm .

The zirconia sample was tested using microflotation and was found to be completely hydrophilic. The CMC used was DEP 267 (supplied by Akzo Nobel), with a molecular weight of approximately 350 000 g/mol.

Yield stress measurements

Yield stress measurements were performed using a Physica MC 1+ rheometer, in conjunction with a double gap measuring geometry. The gap size used was 0.5 mm. Minerals were placed in 10^{-2} M KNO_3 solution, to make up a suspension with volumetric solids fraction (ϕ) of 0.54. The solution pH was varied from pH 9.5 to pH 2 with nitric acid. Rheograms were generated in the shearing rate range between 50 and 150s^{-1} . The yield stress values were calculated using the Casson model (Equation 1), where τ is shear stress, γ is shearing rate, while τ_C and η_C are Casson yield stress and viscosity respectively.

$$\sqrt{\tau} = \sqrt{\tau_C} + \sqrt{\eta_C \cdot \gamma} \quad (1)$$

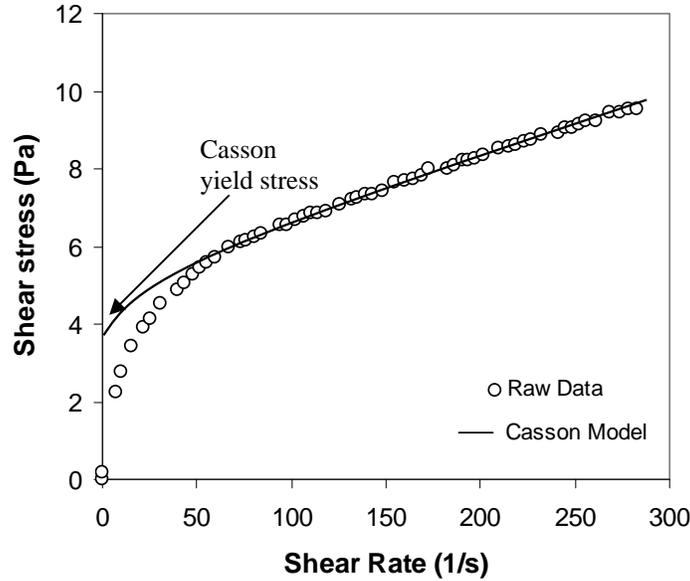


Figure 1 – Rheogram of a suspension of zirconia fitted with a Casson model

Point of zero charge measurements

The point of zero charge of talc minerals was determined using the Roberts-Mular titration method [23]. This method relies on the principle of ion exchange between the mineral and solution medium, as opposed to the physical mobility of a particle in solution in electrokinetic techniques. There is currently no mathematical model that interprets the electrophoretic mobility of plate-like anisotropic particles, and it is important to point out that the applied Roberts-Mular method is independent of the shape factor of the particles.

In this method, the pH of a suspension is measured at different ionic strengths of the solution. The difference in the initial and final pH values is measured and plotted versus the final solution pH. The point where the ΔpH value equals zero indicates the pH of the point of zero charge of the mineral. The supporting electrolyte used in these tests was KCl, and the concentration was varied between 10^{-2} and 10^{-1} M. The solution pH was adjusted using hydrochloric acid.

Intrinsic viscosity measurements

The intrinsic viscosity measurements were performed using a Lauda Viscometer, in conjunction with a three-tube Ubbelohde capillary. The polymer solutions were made at varying concentration, with 10^{-2} M KNO_3 as supporting electrolyte. The pH of the solutions was adjusted drop-wise with nitric acid and KOH. The reduced viscosity (η_{red}) and intrinsic viscosity ($[\eta]$) values were calculated using the Huggins equation [20] (Equation 2), where η_{rel} is the relative viscosity of the solution, c is the solution concentration and κ is the Huggins coefficient.

$$\eta_{red} = [\eta_{rel} - 1]/c \quad (2a)$$

$$\eta_{red} = [\eta] + \kappa[\eta]^2 c \quad (2b)$$

RESULTS AND DISCUSSION

Colloidal behaviour of isotropic and anisotropic suspensions

The rheological behaviour of the suspensions of both zirconia and talc, at similar solids volume fraction, as a function of pH was studied and the yield stress values were calculated using the Casson model. Figure 2 shows that the two suspensions exhibit similar rheological behaviour.

Both curves exhibit peaks in a similar pH range (pH 5.5 – 6). The magnitude of the peaks is equally similar, at approximately 1.8 Pa. The suspensions have the same volumetric solids fraction ($\phi = 0.54$) and a similar size distribution. Therefore, one cannot distinguish between an isotropic and anisotropic mineral behaviour based solely on the rheological measurements. However, the differences become more apparent when rheological information is viewed in conjunction with the electrophoretic and point of zero charge data for both minerals. The apparent electrophoretic isoelectric point of New York talc is well documented [14, 15, 18, 24] and the general agreement is that it lies at $\text{pH} \approx 2.5$. The isoelectric point of zirconia shows variation depending on the source of the mineral, but has been quoted to lie in the range between pH 6 and pH 7 [2, 3].

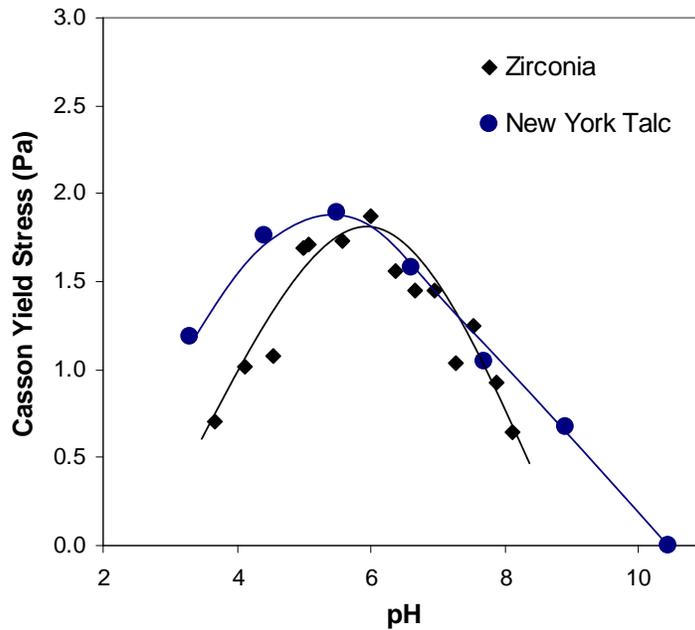


Figure 2 – Casson yield stress of talc and zirconia suspensions, showing the similarity in the behaviour of the two suspensions

Points of zero charge of both talc and zirconia suspensions were measured using the Roberts-Mular titration method. The results shown in Figure 3 confirm that the point of zero charge of zirconia lies at $\text{pH} \approx 6.5$. This value falls within range of the electrophoretic isoelectric points of zirconia quoted in literature. However, in the case of talc, the point of zero charge lies at $\text{pH} \approx 7.7$. This point is significantly different from the accepted apparent isoelectric points, measured using electrophoretic techniques.

Table 1 shows the comparison between the zeta potential, Roberts - Mular titration and yield stress measurement for both isotropic zirconia and anisotropic talc. The results demonstrate that in case of zirconia, all three values converge, as is expected for isotropic minerals. This is not the case for talc where the values vary over a wide pH range.

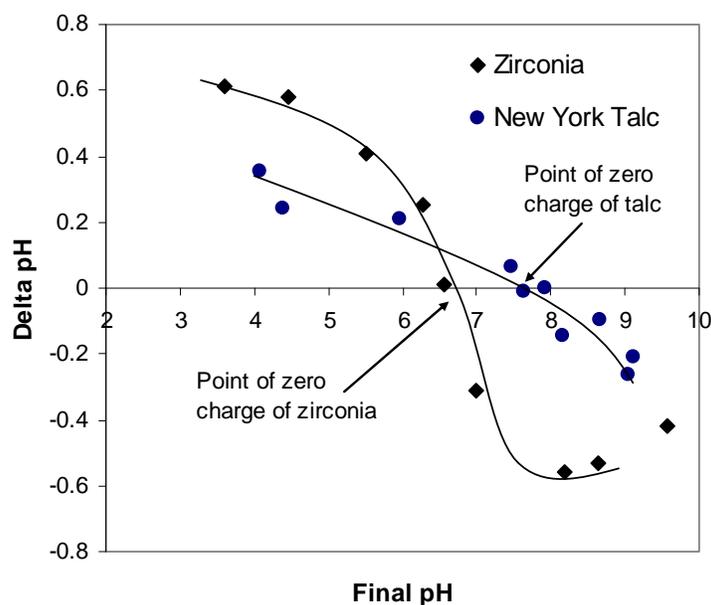


Figure 3 – Roberts – Molar titration of zirconia and New York talc (concentration of electrolyte varied between 10^{-2} & 10^{-1} M)

Table 1 – Comparison between the characteristics of suspensions of talc and zirconia, reflecting their surface properties

Reported Values	pH – Talc	pH – Zirconia
Isoelectric point	2.5	6 – 7
Point of zero charge	7.7	6.5
Aggregation Peak	5.5	6

Effect of CMC addition on isotropic and anisotropic mineral suspensions

As shown previously, rheological measurements could not distinguish between the behaviour of isotropic zirconia and anisotropic talc on their own. However the differences become more evident with the addition of anionic polymer to the solution. The effect of CMC addition on suspensions of isotropic zirconia is shown in Figure 4. The results reveal that at high pH a strong decrease in the yield stress values is observed, indicative of a strong dispersive force. This is likely to result from an increase in negative charge on the mineral surface, creating stronger inter-particle repulsive forces.

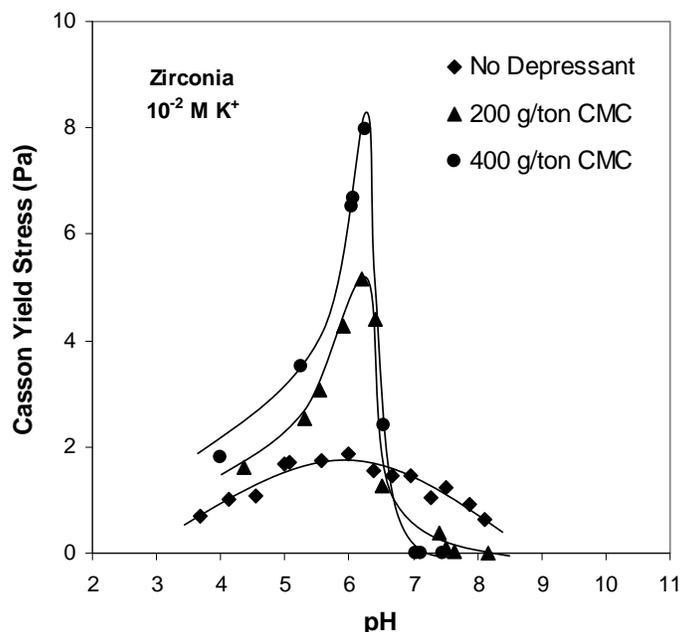


Figure 4 – Effect of CMC addition on zirconia suspensions

At lower pH values the situation is very different. As soon as the suspension reaches the point where the pH approaches that of the point of zero charge, the yield stress curve undergoes a sharp increase, reaching a yield stress value far exceeding that achieved in the absence of polymer. This is an interesting effect, because it indicates that an additional attractive force is present other than van der Waals force.

The increase in the magnitude of the peak could be explained by the incomplete coverage of weakly positive zirconia particles by the negative polymer molecules. The incomplete coverage would result in the presence of both positively charged and negatively charged zones on the particle which would in turn cause the suspension to hetero-coagulate. However the increased peak obtained at 400g/t CMC addition suggests that there may also be other interactions occurring causing the increased coagulation at these conditions and this should be further investigated.

At pH values below 5 the suspensions still exhibits a yield stress value higher than that in the absence of polymer. This once again could be explained in terms of DLVO theory, whereby the overall strong positive charge of the particles is replaced by a weaker negative charge of the polymer. This could cause the overall repulsive forces in the suspension to be diminished, resulting in the suspensions becoming more coagulated. This result is especially important, because carboxymethyl cellulose is generally considered to be a dispersant. These results show that CMC is able to act as a strong coagulant under certain circumstances and this effect also requires further investigation.

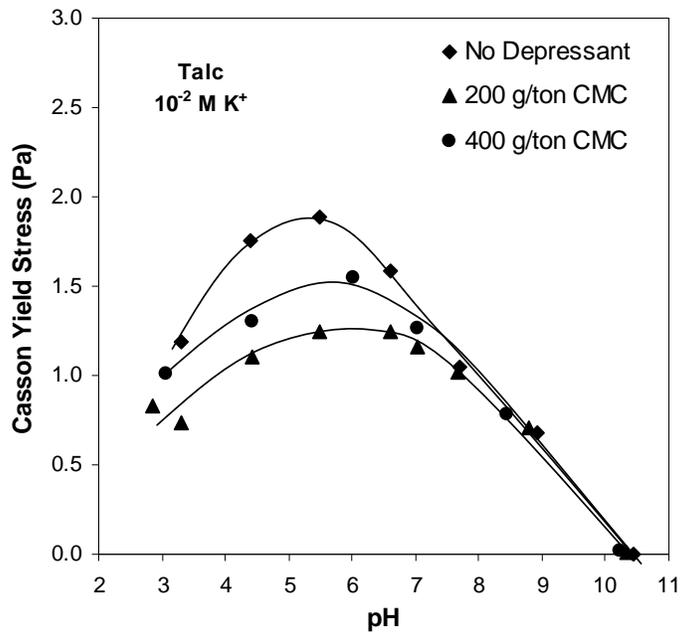


Figure 5 – Effect of CMC addition on the rheology of talc suspensions

Figure 5 shows the rheological behaviour of anisotropic talc suspensions as a function of pH and CMC addition and that the rheological behaviour of talc was only affected by the addition of CMC at pH below ≈ 8 . The addition of CMC decreases the yield stress of the suspension, which is indicative of the increased degree of dispersion and it is likely to result from adsorption of CMC and increasingly negative electrical charge of the interacting particles. This pH value coincides with the apparent point of zero charge of talc found by means of a Roberts – Mular titration (see Figure 3).

It is important to note, that in the case of talc suspensions, although polymer addition has little effect on the rheology of the suspensions in the region where the particle edges are thought to carry a negative charge, previous research has shown that CMC does adsorb onto talc in that pH region [18] and talc floatability is reduced [15, 25] This has been explained by hypothesising that electrostatic attraction plays a significant role in CMC adsorption mechanisms. This would make adsorption weaker in the regions where minerals carry a negative charge, to the point where it might not reflect on the rheological behaviour of the suspension [9].

However this is not the case of zirconia suspension, where the strong effect of polymer addition is evident at high pH values, where the mineral is strongly negative. In order to verify the electrostatic bonding hypothesis one would have to compare the relative magnitudes of the negative charge on the surfaces of both talc and zirconia. While zeta potential measurements can be used to measure the surface charge of isotropic zirconia, one

cannot use the same measurement for plate-like anisotropic minerals. This is due to the fact that there is no mathematical model currently in existence that relates particle surface charge of such particles to their electrophoretic mobility, as made evident by Dukhin and Derjagun [26].

Effect of pH on the conformation of CMC

As mentioned previously, many researchers have explained the differences in the adsorption characteristics of CMC's onto minerals as a function of pH, by the effect that pH might have on the conformation of the polymer molecules and thus causing the adsorption density to change as a result [14, 18]. Therefore, it is important to measure the degree of coiling of the polymer molecules as a function of pH to make sure that the different results do not arise as a function of polymer configuration. Intrinsic viscosity measurements were used to determine the degree of coiling of the CMC molecules in the pH range used in the rheological experiments. Figure 6 shows the reduced viscosity of the solutions of CMC as a function of decreasing solution concentration. According to Huggins equation (equation 2), the intrinsic viscosity is equal to the reduced viscosity of the solution as the polymer concentration approaches zero. Therefore, the intrinsic viscosity is given by the intercept of the straight line fit of the reduced viscosity data, while the Huggins coefficient (κ) is given by the slope of that regressed line.

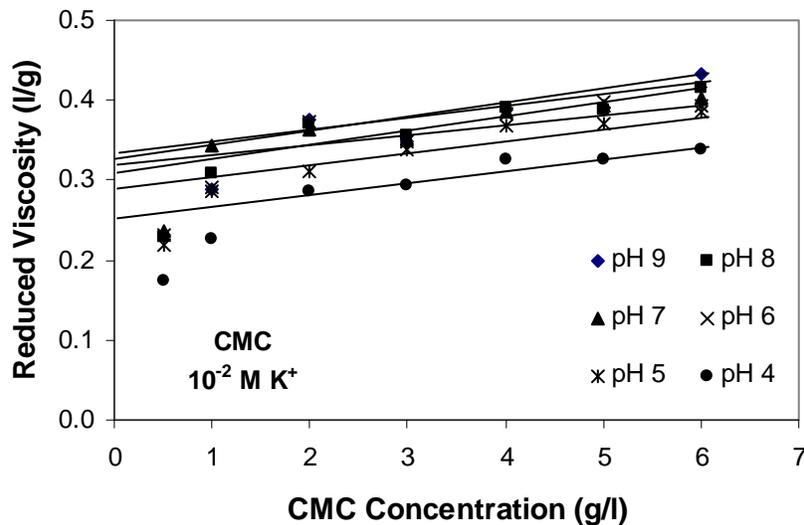


Figure 7 – Relative viscosity of CMC solutions as a function of pH and CMC dosage

Figure 7 shows the resultant intrinsic viscosity of this particular CMC as a function of pH. The error bars indicate a 95% confidence interval, determined from the quality of the linear regression shown in Figure 6. The results show that the intrinsic viscosity of CMC remains consistent above pH 6. However, as the pH moves below 6 the intrinsic viscosity begins to diminish, indicating a greater amount of coiling of the CMC molecules. However, the change is very small and does not extend far outside the confidence interval. The change of this magnitude is unlikely to account for the magnitude of changes that took place on the mineral surface as a function of pH shown in Figures 4 and 5.

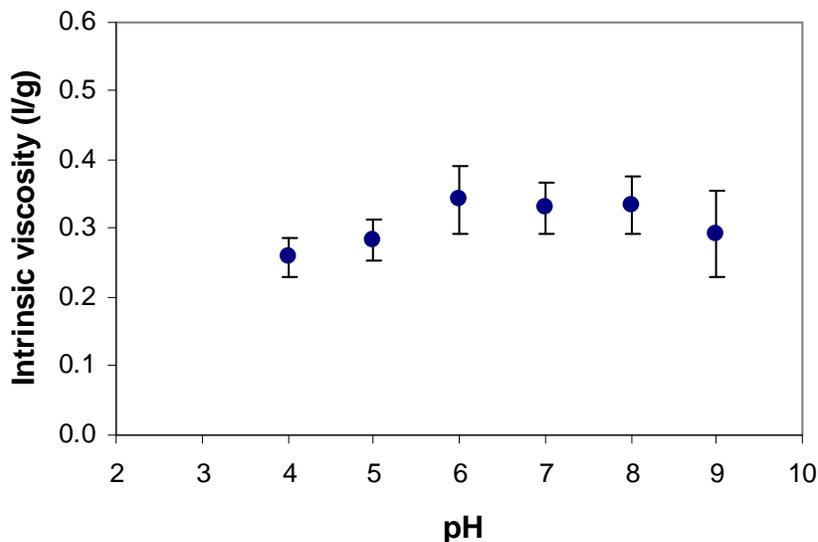


Figure 7 – Intrinsic viscosity of CMC solutions as a function of pH

CONCLUSIONS

From the information presented in this paper, the following conclusions could be drawn:

- In a pure mineral system in the absence of charged polymers, rheological measurements alone are insufficient to distinguish between suspensions of isotropic and anisotropic minerals respectively.
- However, the use of rheological measurements in conjunction with electrophoretic and point of zero charge data makes the differences in behaviour of isotropic and anisotropic minerals more evident. In case of isotropic minerals, the coagulation peak, the isoelectric point and the point of zero charge all converge on the same value. However, for anisotropic minerals, these values are spread out over a wide range.

- The addition of anionic polymer to the mineral suspensions further accentuates the differences in behaviour of isotropic and anisotropic minerals. The addition of CMC was found to significantly affect the rheological behaviour of talc suspensions in the acidic pH range. The addition of CMC decreases the suspension yield stress, which is indicative of a greater degree of dispersion of the suspension.
- The addition of CMC was found to have a significant effect on the rheological behaviour of zirconia suspensions in the entire pH range. At high pH the addition of CMC resulted in a decrease in yield stress values, but at a slightly acidic pH it caused a dramatic increase in the yield stress values. This means that CMC should not be simply labelled as a dispersant. It may have strong coagulating properties under certain circumstances.
- Intrinsic viscosity measurements showed that the changes in the rheological behaviour of both minerals are due to the differences of surface charge distribution as opposed to conformational changes of in polymer solutions.
- The study of other minerals such as those that do not have clearly defined crystal structures, such as Scotia talc, as well as mixtures of minerals could provide further information as to the effect of CMC addition to mineral suspensions.

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