

The Effect of pH and Ionic Strength on the Bulk and Interfacial Properties of Starches

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Abstract: A combination of UV spectroscopy and turbidity techniques were used in this work to examine the effects of pH and salt (type and concentration) on the bulk and interfacial properties of starch and anthracene labelled-starch. The study of starch interaction with monovalent, divalent and trivalent cations revealed significant differences in turbidity values (Td). The exchangeable cations working in this study are Al³⁺, Ca²⁺, and Na⁺ in order of decreasing valency. An interpretation of the gained results suggests that Td is significantly affected by the valency and size of the interacted cations. A decrease in the valency of the cations is combined with a sharp decrease in the Td values, whereas, for a constant valency an increase in the turbidity of starch solution was recorded in this order I⁻ > Br⁻ > Cl⁻, this was credited to that the halogen atom radius becoming bigger. By adding more halide salt (NaX) the Td values were sharply decreased because of the direct interaction between the X⁻ ions and hydrogen in hydroxyl group of starches. On the other hand, an increase in the turbidity values were observed at high alumina content, however increasing the pH was a combined with a decrease in the turbidity. The absorbance data for anthracene labelled starch adsorbed onto alumina agreed with the turbidimetric measurements. Finally, adding calcite also lead to an increase in the turbidity but decreasing the pH caused an in a decrease in the turbidity.

Keywords: Starch, anthracene labelled starch, interfacial properties, turbidity

1. Introduction

Starch is annually renewable natural resource, an abundantly obtainable, low-cost polyhydroxy polymer. Because of these beneficial properties, there has been substantial research for investigating such a biodegradable material [1]. The starch configuration consists of two types of chains, linear amylose and branched amylopectin (see Figure 1). Depending on the botanical source, starch usually contains about 20 % amylose and up to 80% amylopectin by weight [2], but starch contains 80% of amylose and 20% amylopectin can be available [3].

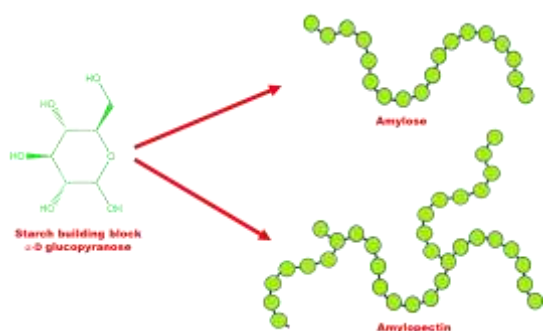


Figure 1: Linear (amylose) and branched (amylopectin) of starch

Pure starch is soluble in warm water via forming hydrogen bonds between hydroxyl moieties and aqueous medium. Starch solution can be utilized as a thickening, stiffening or gluing agent. The main industrial non-food usage of starch is as an adhesive material [4]. Upon starch mixing with metals in basic or acidic aqueous solution, mainly strong electrostatic interaction controls their interaction, whereas, H-bonding and hydrophobic forces play vital role in neutral polysaccharides reaction [5]-[7]. In our previous work [3], [8], we have reported that the adsorption behavior of starch and modified starch onto minerals, such as silica and ferric chloride, is mainly ruled by factors like solution pH and

concentration, still the effect of presence of multivalent cations and anions on molecular interactions of starch in bulk and at solid interference are not fully understood. Nevertheless, it is common that starch chain swells at higher pH, due to electrostatic repulsion between ionized starch hydroxyl groups [9], [10]. In addition, the starch hydroxyl moieties bind to mineral surfaces via hydrogen bonding or chemical interaction [7]. The stability of adsorbed polysaccharides at solid surfaces is controlled by the structure adopted by their chains [11].

Building on our continuous work in introducing starch as a powerful biomaterial can be applied for water purification, we aim to re-examine the interaction between starch and salts.

2. Experimental

2.1 Materials

All materials were used without further purification, starch soluble pure (Riedel-De Haenag Seelze-Hannover), distilled water, hydrochloric acid (36% HCl) (Sigma), sodium hydroxide (NaOH) (Sigma), alumina (Al₂O₃) (Riedel-De Haenag Seelze-Hannover), sodium chloride (NaCl) (Himited Laboratories Limited), calcium carbonate (CaCO₃) (Riedel-De Haenag Seelze-Hannover), sodium bromide (NaBr) (PKD For Midleks), sodium iodide (NaI) (BDH, Analar-Bdh Chemicals Ltd Poole), calcium chloride (CaCl₂) (Riedel-De Haenag Seelze-Hannover), aluminum chloride (AlCl₃) (PKD For Midleks), and anthracene labelled starch was prepared according to our previous procedure published elsewhere [3], the labelling reaction is summarized in Figure 2.

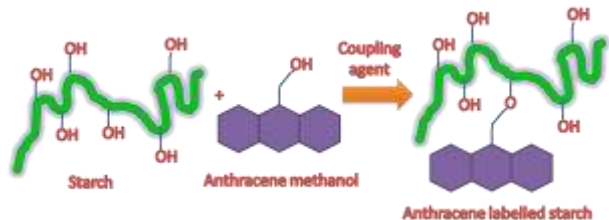


Figure 2: Labeling reaction of starch with anthracene methanol

2.2 Turbidity measurements for starch in bulk solution:

Starch solutions were prepared by dispersing a specific amount from starch in about 1000 ml distilled water. The pH was about 8 for all the starch solutions. Exact amount of salt was added to any solution. The transmittance of the solution was measured on a conventional turbidity meter (Lamotte 2020 We Turbidimeter). Each measurement was repeated three times at room temperature, with duration of 10 minutes for each run. Calibration was done once every day meter is used prior to beginning analysis.

2.3 UV spectroscopy and turbidity measurements for starch-mineral interface:

The correct quantities of each starch and labelled starch was measured and mixed with different mineral content, and then the pH of the sample adjusted to the required value. The mixture was shaken for 18 hours to ensure that adsorption had reached equilibrium. The solution was then left for 6 hours to deposit the solid phase from the aqueous phase. The ultraviolet (UV) spectra were recorded with a Perkin–Elmer spectrophotometer of anthracene labelled starch mineral solution. The scan was done from 290 nm to 400 nm with a scan speed of 400 nm/min. The absorbance value was determined at maximum absorption intensity at 365 nm. Alternatively, the turbidity (Td) analysis was carried out of native starch mineral solution. Absorption intensities were expressed in arbitrary units (a.u), while turbidity values are expressed in nephelometric turbidity units (NTU).

3. Results and Discussion

It is well known that presence of salts in water affects its clarity [12], [13]. A turbid water appears because of the aggregation effect of salts upon increasing their concentration in aquatic system [13]. Presence of suspended materials cause in salt ions-particles binding, this lead to an increase in their weights and consequently their chance of settling to the bottom, see Figure 3. Because of this aggregation, oceans tend to seem in lower average turbidity than other water sources [12], [13]. Building in this natural phenomenon, we introduce herein a naturally occurring biomacromolecule (starch), as a good water clarifier and saver than inorganic and synthetic polymers, since the later could be contaminated with monomers which are very toxic materials [14].

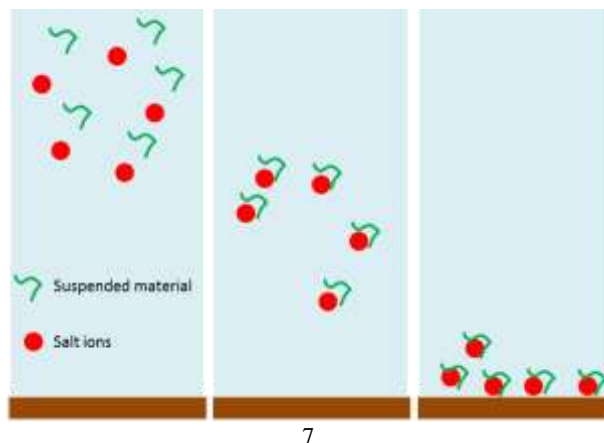


Figure 3: Suspended material can cause salt ions to aggregate and settle at the bottom of a body of water

To do so we have prepared a model saline water system contain a fixed amount from starch, and multivalent salts have been added in different concentrations, as displayed in Figure 4.

As expected adding of NaCl, CaCl₂ and AlCl₃ cause in a sharp increase in water turbidity, this could be attributed to that self-aggregation of small molecules [12], [13] which in turn enhance the scattering of light inside the solution, thus a decrease in the water clarity is observed. Moreover, the turbidity is dramatically influenced by the valency (Al³⁺, Ca²⁺, and Na⁺) and size of atoms of the interacted cations. A reduction in the valency and size of the cations causes a decline in the Td values. As an over all, presence of starch in salt aqueous solution causes a decay in the turbidity of Ca²⁺, and Na⁺ water systems by increasing their concentrations, whereas adding more aluminum chloride make the solution cloudier. This could be elucidated to the strength of binding affinity for (R-OH) starch groups toward mono and di cations rather than tri cations.

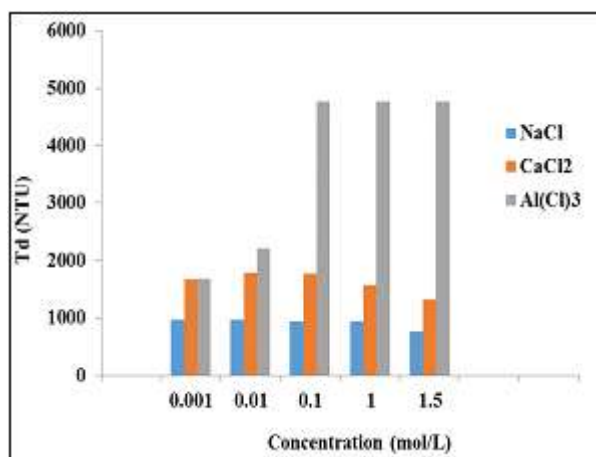


Figure 4: The turbidity as a function of concentration of starch at various kinds of cations

In Figure 5 the valency of cation was fixed by selecting sodium salts of chloride (Cl), bromide (Br) and iodide (I). As it can be noted at the beginning a rise in the turbidity of starch solution was recorded in this order, I⁻ > Br⁻ > Cl⁻, this could be attributed to that the halogen atom radius becoming bigger in that direction. By adding more halide salt (NaX) the

Td values were dramatically declined, this could be attributed to the presence of direct interaction between the X⁻ ions and hydrogen in hydroxyl group of starches [15].

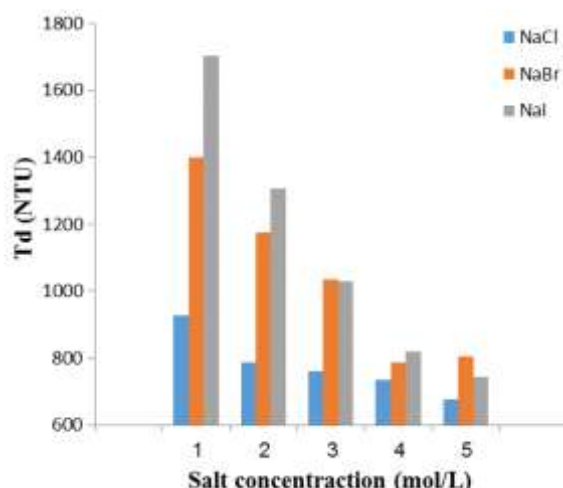


Figure 5: The turbidity as a function of concentration of starch at various kinds of anions

The interfacial properties of starch onto mineral surface are displayed in Figures 6 and 8. When the starch alumina interface was studied (Figure 6) an increase in the turbidity values were noted upon adding more alumina, whereas increasing the pH lead to a decrease in the turbidity values, this obtained results proposed that electrostatic interactions were mainly responsible for the adsorption of starch on mineral surface. In our previous work the interaction of oppositely charged material was described in detail [3]. To support the result gained from the turbidity technique, UV-spectroscopy analysis was carried out. Because the native starch is weak photo-active polymer, we have successfully labelled the starch chain with anthracene methanol to monitor the interfacial behavior of the starch at alumina surface. The first profit of using anthracene is that it can be covalently coupled the to the polymer chain in suitably small amounts so that they do not disturb the conformational behavior of starch [3]. The other benefit is that the photo-response of the covalently attached anthracene label can be directly correlated back to the starch itself [3]. Figure 7 shows the maximum absorbance of anthracene-labelled starch mixed alumina solutions at numerous pH values, an increase the absorbance as the pH decreased to 7 indicates that more starch chains remain in the bulk solution, but at pH 9 and 11 the decrease in the absorbance can be explained as more anthracene-labelled starch was attached onto the mineral surface and little was remained in the bulk solution, this tendency agrees with the turbidity results.

Despite Figure 8 shows fluctuated pH dependence of the starch adsorption onto calcite (CaCO₃), adding CaCO₃ similarly lead to an increase in the turbidity but as an overall decreasing the pH caused an in a decrease in the turbidity, which could be because of increasing in the amount of adsorbed starch.

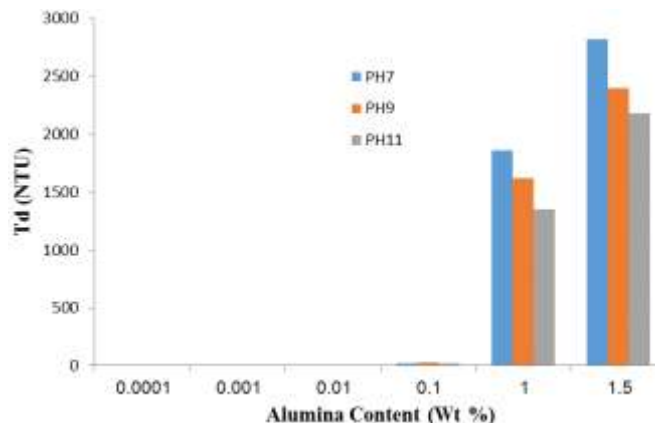


Figure 6: Effect of pH on the turbidity of the starch-alumina interface in aqueous system

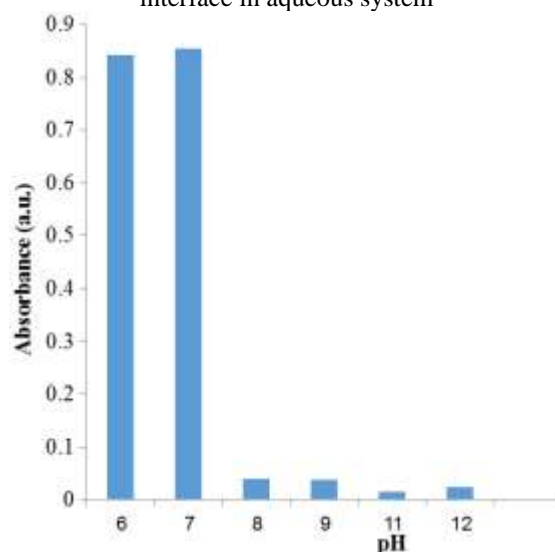


Figure 7: Maximum absorbance of aqueous anthracene-labelled starch (10⁻¹ Wt%) and alumina (1 Wt%) solutions at various pH

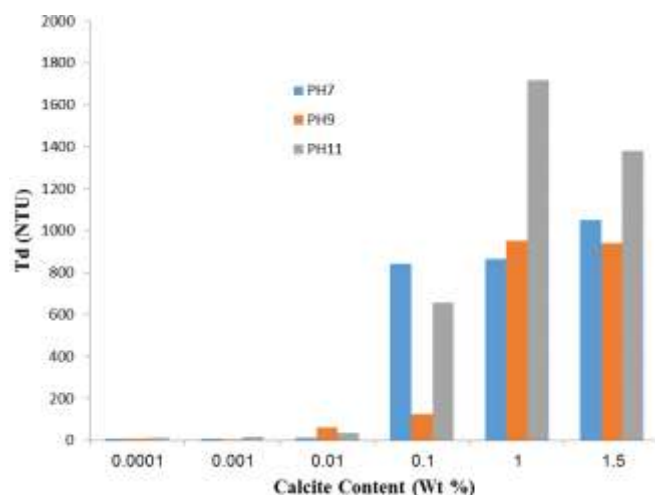


Figure 8: Effect of pH on the turbidity of the starch-calcite interface in aqueous system

4. Conclusions

When starch mixed with various salt aqueous solutions, the turbidity and UV-spectroscopy results suggest some interactions between starch and small molecule. In brief, existence of starch in salt aqueous solution causes a decrease

in the turbidity of Ca^{2+} , and Na^+ water systems, however a cloudy solution is appeared in the presence of Al^{3+} . This could be attributed to the strength of binding affinity for starch hydroxyl groups to mono and di cations rather than tri cations. At fixed cation, an increase in the turbidity of starch solution was noted in this order, $\text{I}^- > \text{Br}^- > \text{Cl}^-$. Adding more NaX salt was accompanied with a decline in the turbidity, this was due to a direct interaction happened between the X^- ions and hydrogen in hydroxyl group of starches. At the adsorbed starch onto alumina, increasing the pH caused a decrease in the turbidity and absorbance values, which indicated that more starch was attached onto the mineral surface and tiny was remained in the bulk solution. On contrary, decreasing the pH caused an in a decrease in the turbidity when the starch was blended with calcite.

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