

## Aggregation studies of *pinus radiata* wood extractives under increased system closure.

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### SUMMARY

Within the pulp and paper industry, the recycling of process water to reduce water consumption leads to accumulation of colloidal Material in this water and greater risk of deposition. A major factor in the colloidal stability of these substances, which arise from the wood extractives, is the presence of natural polymers originating from the wood as well as salts that accumulate in the process water as a result of increased system closure. This work explores the factors that affect the stability of wood extractive colloids under varying conditions of ionic strength, ionic valency, shear, pH, mixtures of cations and wood polymers released from *pinus radiata* thermomechanical pulp.

Coagulation of a colloidal wood extractive solution by a single salt was found to follow the Schultz-Hardy rule, with the critical salt coagulation concentration (CCC) strongly influenced by salt valency ( $z$ ). Changes to both pH and shear experienced by the colloid, were observed to affect the concentration of salt required to destabilise the colloid. However, on addition of a second salt to the solution, the CCC decreased for calcium + sodium in comparison to when only a single salt was present.

Addition of wood polymers to an aqueous dispersion of wood extractives caused two stages of destabilization of the wood extractive colloids, which were separated by an apparently stable region. The behaviour was typical of aggregation by polymers in which polymer bridging at low polymer additions caused firstly colloid destabilization, followed by steric stabilisation of the colloids at medium concentration of the polymer, then depletion flocculation followed finally by depletion stabilization at higher polymer concentrations.

### KEYWORDS

wood extractives, pitch, aggregation, photometric dispersion analyzer, critical coagulation concentration, polysaccharides, shear

### INTRODUCTION

White water in the pulp and paper process is a complex mixture of naturally occurring substances leached from the wood, additives used to stabilize these substances, inorganic chemicals arising from brightening the pulp and fillers added to the paper. The lipophilic wood extractives that are released from the wood during pulping form soft colloidal substances which are known to deposit throughout the paper mill. To control these naturally occurring substances, it is essential to develop an understanding of the effect that the other components have on the colloids.

The stability of colloidal wood extractives is very dependent on the attractive and repulsive forces that exist between the colloidal particles. Stability is achieved when the repulsive forces are greater than the attractive forces while destabilization and aggregation of the colloids occurs when the repulsive forces are reduced sufficiently for the attractive forces to dominate. The repulsive forces arise from the negative charge on the particles and the resulting redistribution of the ions in solution that form an electrical double layer. The charge on wood extractive colloids comes about from the presence of carboxylic acid groups which will deprotonate and so ionize the colloid as pH is increased (1).

There are several factors that affect the colloidal stability of the wood extractive particles and their aggregation. One of the main factors is the presence of electrolytes. Electrolytes in solution influence the electrical double layer and in some cases, the surface charge. At high electrolyte concentration, the thickness of the electrical double layer is compressed (2). A critical electrolyte concentration, known as the critical coagulation concentration (CCC), exists at which the colloid is completely destabilized. Numerous studies have been undertaken to determine the CCC for a range of salts for wood extractive colloids (3-5). Although there are some differences between the reported values, generally the CCC is highly dependent on the valency of the destabilizing electrolyte (2, 6). An understanding of the effect of increasing salt levels on wood extractive colloidal stability is essential, particularly when most mills are undertaking increased recycling of process water in order to reduce water usage.

Another important factor found to influence the colloidal stability of wood extractives is the presence of dissolved polysaccharides originating from the wood. These polysaccharides have been shown to interact with the wood extractives and significantly affect colloidal stability by stabilizing them in solution (7-11). Other factors that influence aggregation and colloidal stability include shear, presence of other additives such as polymers and the chemical composition of the material in the colloids.

Aggregation of wood extractive colloids has been studied in a number of different ways, including direct deposition measurements (12-16), and counting of pitch particles (15, 17). The kinetics of aggregation

of colloidal particles such as wood extractives, under dynamic shear conditions, has also been investigated using a Photometric Dispersion Analyzer (PDA) (18-25). Use of a PDA makes it possible to look at both the growth and distribution of colloid sizes (22).

This paper explores the factors that affect the aggregation of wood extractive colloids from *pinus radiata*. The effect of various salts, shear, pH and polysaccharides are investigated using a PDA to study the aggregation kinetics, stability factor and the CCC of different electrolytes. The effect of multiple salts is also investigated in order to better understand the effect of mixtures of cations that are present in a typical mill situation along with polysaccharides and other substances, all competing and interacting with each other and the wood extractives. A basic understanding of the interactions between all the factors is needed in order to allow the mill to develop strategies to deal with increased wood extractives and other substances that affect their stability with reduced water usage and increased system closure.

## EXPERIMENTAL

### Materials

All electrolytes used were dissolved in distilled water as stock solutions. Constant volumes were added to the PDA solution with desired concentration of stock solutions, such that the final volume (300 mL) had the required concentration of salt. Salts of  $\text{CaCl}_2$  and  $\text{KNO}_3$  were purchased from BDH at 99.8% purity.  $\text{NaCl}$  and  $\text{Al}_2(\text{SO}_4)_3$  (99.8%), were obtained from Merck.

A thermomechanical pulp (TMP) from *pinus radiata* was collected from the primary refiners at Norske Skog, Boyer, Tasmania.

### Preparation of wood extractives

TMP was freeze dried and soxhlet extracted with hexane. The hexane was removed by rotary evaporation to obtain the neat wood extractives (stored at  $-4^\circ\text{C}$  until needed). The composition of the wood extractives is shown in Table 1.

Table 1: Composition of wood extractives from *pinus radiata* (mg/g of dry pulp)

| Fatty Acid | Resin Acid | Triglycerides |
|------------|------------|---------------|
| 1.44       | 6.17       | 5.89          |

Aqueous wood extractive dispersions were prepared by dissolving 500 mg of wood extractives in 50 mL acetone (99.5% purity, Chem.- Supply) and adding this to 1500 mL distilled water containing 1 mM  $\text{KNO}_3$  with pH adjusted to 5.5 (with 0.5 M  $\text{HNO}_3$ , BDH). The dispersion was dialysed for 24 hours using cellulose membrane tubing with a molecular mass cut off of 12,000 amu (Sigma-Aldrich D9402-100FT) to

remove acetone. The wash water, containing 1 mM  $\text{KNO}_3$  adjusted to pH 5.5, was changed every hour for the first 5 hours. Due to sample loss during dialysis final concentration of extractives is in the region of 100 mg/L.

### Preparation of extracted wood polymers

Extracted wood polymers were obtained by soxhlet extraction of *pinus radiata* TMP following the procedure of Johnsen (26). The pulp was disintegrated in water at 2% consistency at  $60^\circ\text{C}$  for 3 hours, repeating this process up to 5 times after filtering the wet wood fibre. The solution was then concentrated through air drying. This dispersion was dialysed for 24 hours in 1 mM  $\text{KNO}_3$  with pH adjusted to 5.5 to remove unwanted material. Dialysis was conducted using a cellulose membrane tubing (Sigma D-9402, 76mm wide, >12,000 MW).

The chemical composition of the wood polymers is shown in Table 2.

Table 2: Chemical Analysis of wood polymers

|                                     |                                     |
|-------------------------------------|-------------------------------------|
| Carbohydrate                        | 14.3 $\pm$ 0.3<br>mg/g dry<br>pulp  |
| Lignin                              | 1.14 $\pm$ 0.03<br>mg/g dry<br>pulp |
| total sugars                        | 10.8 $\pm$ 1.5<br>mg/g dry<br>pulp  |
| Cationic Demand mmol/g equiv charge | 0.42                                |
| galactose: glucose: mannose         | 0.4: 1: 2.4                         |

## Methods

### PDA Wood Extractive Aggregation

A Photometric Dispersion Analyzer (PDA 2000, Rank Brothers, Cambridge, UK) was used to monitor the changes in aggregation of the wood extractive colloidal dispersions. The 200 mL solutions were stirred at 500 RPM in a Britt Jar fitted with a 4 cm diameter flat impeller rotor. A peristaltic pump was used to recirculate the dispersions through the PDA at a flow rate of 70 mL/min.

The instrument was initially calibrated with distilled water and the DC gain control was adjusted to give a DC value of 10 V (22, 27). The turbidity fluctuations of a flowing suspension under controlled shear conditions were recorded by the PDA. The ratio of the root mean square (RMS) of the AC voltage to the DC voltage was monitored as a function of time. Three replicates were measured for each condition. The PDA signal was smoothed using a 40-point moving average.

## RESULTS AND DISCUSSION

### Critical Coagulation Concentration

The effect of salt concentration and the salt itself (NaCl, CaCl<sub>2</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) on the aggregation of wood extractive dispersions was studied using a PDA. At the on-set of aggregation with salt addition, there is a linear increase in the PDA output as shown in Figure 1 before the signal stabilizes. This initial PDA slope of aggregation is related to the coagulation constant or stability ratio (W) (28). The stability ratio (W) is determined from the experimental results of the aggregation kinetics by the relationship,

$$W = \frac{k_{fast}}{k_i} \quad (\text{Eq. 1})$$

where  $k_i$  is the slope of a particular salt and  $k_{fast}$  is the fastest response to the addition of a salt.

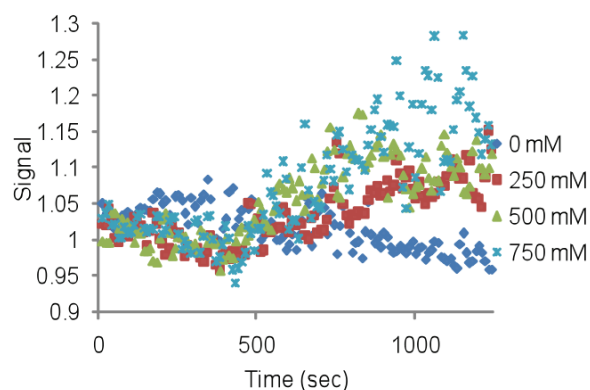


Figure 1: The response of wood extractives to the addition of various concentrations of NaCl.

Figure 2 shows the stability curves for the three salts studied. These are obtained by plotting log W as a function of salt concentration (logarithmic scale). Sigmoidal curves with three distinct regions are observed:

1. an initial flat region at low salt concentration (a stability zone),
2. a region in which Log W decreases rapidly (a transition zone of colloidal instability); and
3. a region in which Log W is 0 at higher salt concentration (complete aggregation of the colloid).

The critical salt concentrations, (CCC), for each salt, determined by extrapolating the slope of the linear transition to the x-axis, are summarized in Table 3.

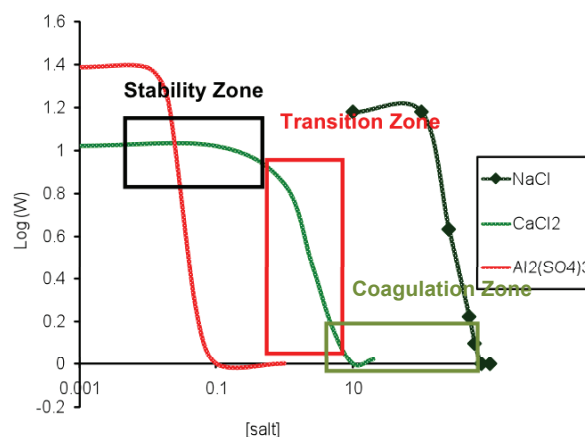


Figure 2: Wood extractive stability curves under dynamic conditions for various electrolytes (pH 5.5, 23°C).

Table 3: Wood extractive Critical Coagulation Concentration (CCC) under dynamic conditions for different electrolytes at pH 5.5.

| Salt             | CCC (mM) |
|------------------|----------|
| Na <sup>+</sup>  | 720      |
| Ca <sup>2+</sup> | 7.8      |
| Al <sup>3+</sup> | 0.065    |

The results in Figure 2 and Table 3 show a strong dependence on the salt valency. The transition in the curves and the CCC values for the monovalent electrolytes occurs at a concentration around two orders of magnitude higher than that of divalent salts and similarly for the trivalent ions compared to divalent ions. A linear relationship between the CCC and cation valency was obtained as shown in Figure 3. The Shultz-Hardy rule predicts the critical coagulation concentration (CCC) to vary inversely with the sixth power of the cation valency ( $z$ ) (2). The slope for the line of best fit shown in Figure 3 is -8.3. It is debatable whether or not the slope of the relationship in Figure 3 fully supports the Shultz-Hardy's rule that predicts a slope of -6. However, given that the effect of metal ions can be influenced by other side reactions within the solvent not accounted for by the Shultz-Hardy rule, the resulting CCCs appear to fit reasonably with this theory. Further it can be argued that the discrepancy falls well within experimental error due to the complexity of a non-ideal industrial suspension that is heterogeneous in size, composition and contaminants. The result for the trivalent aluminium ions is a little surprising, given that at the pH investigated, these ions should exist in a number of hydrated forms of varying charge and not strictly in a trivalent form (29, 30).

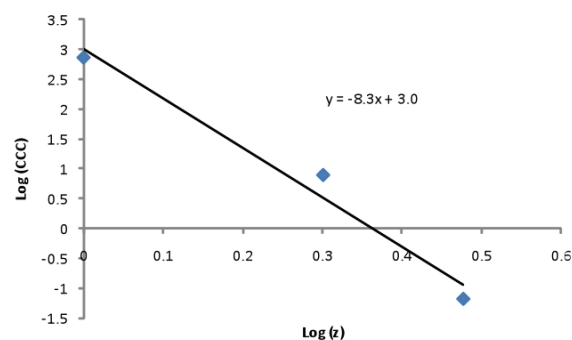


Figure 3: Effect of salt valency on the wood extractives critical coagulation concentration (CCC); pH 5.5 at 23°C and 500 RPM.

It is important for a paper mill to understand where its system is on the stability salt curves. Are they in a region of stability, in a transition region or in a region of complete instability? This information is needed in order to understand how process changes, particularly related to salt concentration, will affect the colloidal stability of the wood extractives. at the Norske Skog Albury mill where water consumption is about 10m<sup>3</sup> per tonne of product cations in white water streams can be around 13 mM for Na<sup>+</sup>, and 3 mM for Ca<sup>2+</sup>, Al<sup>3+</sup> concentrations, at the Tasman mill (where water consumption is > 20 m<sup>3</sup>/tonne of product) can be around 0.06 mM. Although the level of sodium ions is well below its CCC, levels for the divalent and trivalent metal ions are within the transition region of the stability curves shown in Figure 2. This means that the paper mills are operating in critical regions for salt induced coagulation of the wood extractive colloids. Any changes to shear, pH and/or the temperature could induce coagulation and lead to wood extractive deposition.

Factors affecting the CCC

The CCC values obtained in Table 3 appear to be higher for sodium salts than that reported by Sundberg (4), Sihvonen (3) and Mosbye (5), while the calcium value appears to be slightly lower than values reported in the literature and summarized in Table 4. It is noted that the experimental conditions and procedures used in the work reported here are different to those in the cited references and that other factors such as pH and shear may also affect the CCC values. The surface charge and composition of wood extractives may also affect the CCC values for different salts. *Pinus radiata* wood extractives are higher in resin acids than Spruce wood extractives. Sihvonen (3) found that adding dehydroabietic acid to a model Spruce wood extractive dispersion to increase the amount of resin acids present resulted in an increase in surface charge of the wood extractives and increased the stability of the wood extractive colloids.

Table 4: Summary of wood extractive Critical Coagulation Concentrations (CCC) reported for various electrolytes and pH.

| pH  | NaCl (mM) | CaCl <sub>2</sub> (mM) | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (mM) | Reference |
|-----|-----------|------------------------|--|-----------|
| 5   | 150       | 25                     |  | (3)       |
|     | 200       | 10                     | 0.02   | (4)       |
| 5.5 | 100       |                        |  | (5)       |
| 6.4 | 600       |                        |  | (5)       |
| 8   | 500       | 25                     |  | (3)       |

To investigate the effect of shear on the CCC, a series of experiments were undertaken in which the salt- induced aggregation kinetics was measured for wood extractive colloids stirred at two different shear rates. Figure 4 shows the effect of increasing the shear rate of the stirred colloidal dispersion from 350 RPM to 500 RPM and the resulting stability curves and CCC values for NaCl. The CCC decreased from 1040 mM at 350 RPM to 720 mM at 500 RPM. The 500 RPM shear condition used in the Britt Jar to agitate the wood extractive dispersions can be equated to a shear force of 2 x 10<sup>3</sup> s<sup>-1</sup> (31) which is equivalent to the shear forces experienced in the pressure screens and wet end of a modern paper machine.

The effect of shear on the CCC, as observed in Figure 4, may explain the differences in CCC for sodium salts reported by Sundberg *et al* (4) and Sihvonen *et al* (3) as different sample agitation methods were reported. When the samples underwent agitation for a short period of time before concentration determination, the CCC for sodium was found to be 200 mM. By contrast, the CCC for wood extractive colloids subjected to continued agitation was found to be 150 mM for sodium.

Coagulation requires two conditions:

- 1) collision among colloids, and
- 2) high probability of aggregation upon collision.

Increasing shear will increase the rate of collision and so increase the number of collisions occurring in a set time. This will cause an increase in aggregation rate and higher probability of aggregation at lower salt concentrations as the shear is increased.

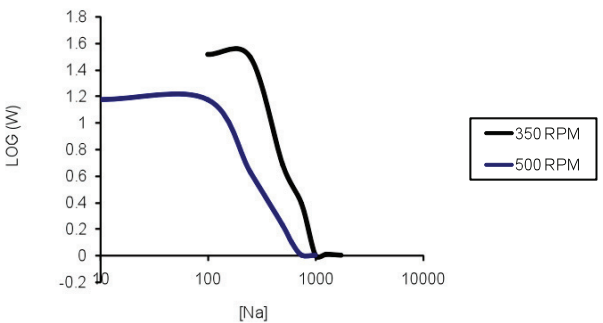


Figure 4: Wood extractive stability curves for various shear rates of sodium (pH 5.5, 23°C).

The effect of pH on colloidal stability at a constant shear was studied using  $\text{CaCl}_2$  as the destabilizing salt. The results in Figure 5 show that as the pH is increased, the stability curve for the wood extractives shifts to the right, indicating greater stability in solution. In turn the critical coagulation concentration for  $\text{CaCl}_2$  increases, from 1.7 mM at pH 3, to 7.8 mM at pH 5.5 and then to 12.1 mM at pH 8. These results indicate that at higher pH's more salt can be present in the process water before complete destabilization of the wood extractive colloids occurs. Part of the reason for the behaviour is that as the pH increases the solubility and charge of the colloidal components also increase and this in turn increases the colloidal stability.

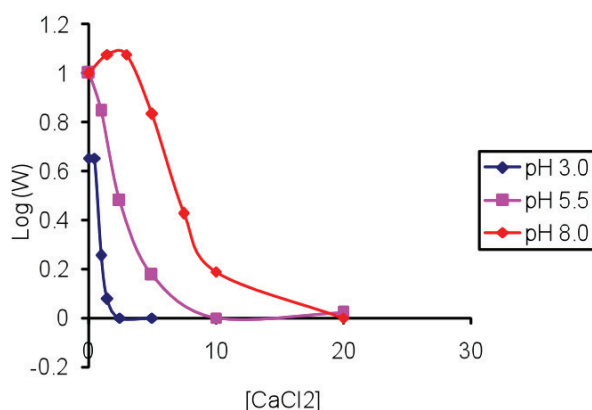


Figure 5: The effect of pH on the stability curve for the effect of  $\text{CaCl}_2$ .

#### Effect of multiple salts present in solution

A number of different salts exist in mill white water, all of which will affect the stability of the colloid. Although the monovalent salts may dominate, the presence of a small amount of divalent and trivalent salts will have a large impact on the colloidal stability as these salts have much lower CCC values as shown in Figure 2 and Table 3. Most studies are based on investigating the effect of a single salt. The effect of a second salt (sodium) on the CCC of a calcium salt was investigated and the results are shown in Figure 6. Several points can be observed from the results. The first is that as the concentration of the second salt (sodium) is increased the minimum in Log W, representing the CCC decreases. The second observation is that the colloids undergo re-stabilization as the concentrations of both salts increase, indicating that the colloid stability behaviour with multiple salts is complex. The effect of the second salt (sodium) on the CCC of calcium is presented in Table 4.

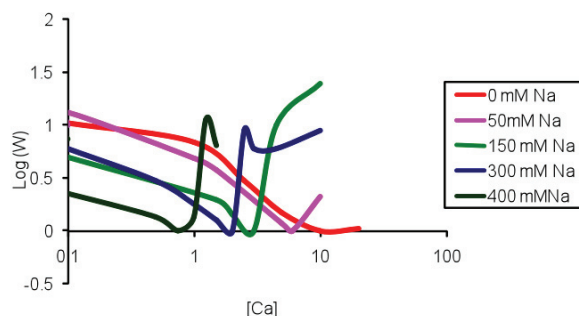


Figure 6: Wood extractive stability curves under dynamic conditions for various concentrations of second electrolyte added to calcium (pH 5.5, 23°C and 500 RPM).

Table 4: Calcium critical coagulation concentrations at different sodium concentrations for wood extractive colloids.

| [Na] mM | CCC [Ca] (mM) | Ionic Strength (mM) |
|---------|---------------|---------------------|
| 0       | 7.8           | 22.8                |
| 50      | 6.03          | 68.1                |
| 150     | 2.96          | 159                 |
| 300     | 2.03          | 306                 |
| 400     | 0.92          | 403                 |
| 722     | 0             | 722                 |

The results indicate that for a paper mill, in which a number of different salts are present in the white water, the critical salt levels at which the colloids will coagulate exhibit a complex relationship and are not strictly additive for the individual salts or based simply on ionic strength. The non linear effect on the CCC due to the second salt is shown in Figure 7.

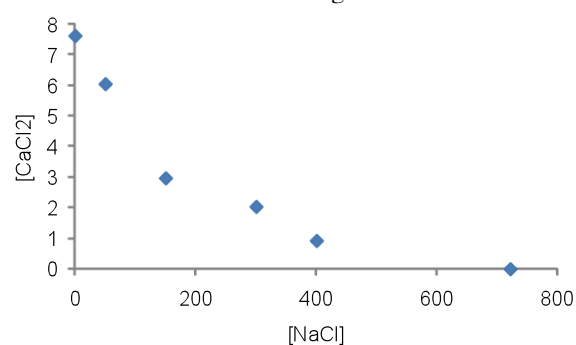


Figure 7: Calcium critical coagulation concentrations in a wood extractive solution with different sodium concentrations.

#### Effect of other stabilizing substances in solution

Literature indicates that the addition of naturally occurring wood polymers to solution stabilizes the wood extractive colloids (7-11). The effect of dissolved wood polymers from *pinus radiata* TMP on



the colloidal stability of *pinus radiata* wood extractives colloids was studied.

Figure 8 shows that at low wood polymer addition (1-10mg/L), destabilization of the colloids occurred. At additions of 10-80mg/L wood polymers, stabilization of the colloids was observed. This behaviour is typical of low polymer additions to solution with destabilization and aggregation of the colloids via bridging flocculation, followed by steric stabilization with polymers anchored to the colloidal surface and at full polymer coverage of the surface (1). At wood polymer additions of 100-400mg/L further destabilization of the colloids occurred followed by a re-stabilization at additions above 400mg/L. Again this behaviour is typical of depletion flocculation and depletion stabilization of synthetic polymers (1). The results indicate that the previously reported (7-11) stabilization of wood extractives by wood polymers is more complicated and very much dependent on the level of wood polymers present. It also indicates that increased accumulation of the wood polymers in papermaking process water may be detrimental to the stability of wood extractives at a particular concentration range of 100-400mg/L.

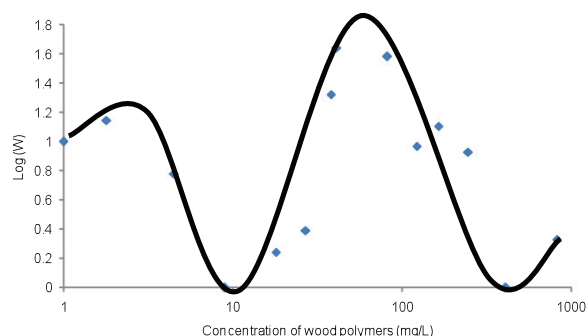


Figure 8: Effect of extracted wood polymers concentration on colloidal wood extractive stability.

## CONCLUSIONS

Colloidal stability of wood extractives is affected by many variables in the paper making process. The critical coagulation concentration (CCC) for wood extractives from *pinus radiata* was found to be slightly higher for sodium salts (612mM) and lower for calcium salts (6.6mM) and aluminium salts (0.1mM) than reported in the literature for Spruce extractives.

Both shear and pH were shown to affect the CCC value. Increasing the amount of shear lowered the CCC due to the effect of shear on increasing the rate of collision and aggregation kinetics. Increasing the pH increased the CCC due to increased solubility and surface charge of the colloids increasing colloidal stability.

The presence of a second salt was found to have a greater effect on lowering the CCC and showed that the relationship was not a simple additive one but more complex. The results highlight the importance for papermakers to have a detailed knowledge of all the salt concentrations in the process water and the combined

effect on colloidal stability. An important finding of the results in relation to increased water closure and build up of salts in solution, was the re-stabilization of the wood colloids at high salt levels.

The effect of wood polymers on colloidal stability of the wood extractives was dependent on the concentration of the wood polymers. The wood polymers were found to act like synthetic polymers in regards to their ability to both stabilize and destabilize the wood extractive colloids.

For paper mills planning to increase system closure a detailed understanding on the potential increase in levels of dissolved salts and wood polymers and the complex effect they have on wood extractives colloidal stability is essential in order to develop strategies to reduce increased deposition problems.

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