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Self-association and aggregation of kraft lignins via electrolyte and nonionic surfactant regulation: stabilization of lignin particles and effects on filtration

Consuelo Fritz, Carlos Salas, Hasan Jameel, Orlando J. Rojas

KEYWORDS: Lignin, Self-association, Aggregation, Colloidal stability, Salt, Surfactants

ABSTRACT: Understanding the aggregation behavior of lignins is relevant to their application, especially toward value-added products. Here we report on the self-association of kraft lignin derived from hardwood and softwood species under mild temperature and pH conditions and in the presence of various salts and surfactants. Besides characterization of lignin functional groups (NMR and others), aggregation (extent and rate) (turbidity, viscosity), surface tension, particle size (dynamic light scattering) and filtration efficiency were determined. Monovalent salt ions increased lignin aggregation while non-ionic surfactants enhanced the colloidal stability of the system by steric effects, depending on the concentration. The combination of salt and surfactant enabled the regulation of the colloidal aggregation and the rheological properties of the respective aqueous dispersions. While pH affects the colloidal stability of lignin in solution, it plays a minor effect on lignin particles dispersed in water, indicating contributions beyond those arising from the presence of carboxylic and phenolic groups. Filtration and separation of lignin from aqueous media (relevant to processing streams, wastewater, etc.), as well as applications that require the control over the stability of lignin can be addressed suitably by application of the simple methods presented here.

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Introduction

Lignin is a biomacromolecule that is attracting renewed interest in several fields (Ago et al. 2012; Norgren, Mackin, 2009; Nypelö et al. 2015; Ogunkoya et al. 2015; Oroumei et al. 2015). Annually, over 70 million tons of lignin are produced worldwide, mainly as by product from the kraft pulping process but only 5% is used in commercial applications (Laurichesse, Avérous 2016). Understanding kraft lignin (KL) colloidal behavior is needed to guarantee suitable uses. Some reasons for the limited use of lignin include the complexity of its structure due to the isolation process and the variability

from different sources, its wide molecular weight distribution, solubility, condensation and re-polymerization after fragmentation, and incompatibility with other polymers or matrices. During the kraft pulping process the aryl-ether bonds in lignin are cleaved (Sjöström 1981) and the residual KL develop more acidic groups (Sjöström 1989). Lignin is soluble in a wide range of solvents such as aliphatic alcohols and acids, methyl and ethyl acetate, acetone, chloroform, dioxane, pyridine, dimethyl sulfide, and tetrahydrofuran. However, KL can be readily dissolved in alkaline conditions (Vainio et al. 2004) and its phase behavior is controlled by temperature, pH, and ionic strength (Norgren et al. 2001). The self-associative behavior of KL has been studied already (Lindström 1980; Lindström 1979; Norgren et al. 2002; Norgren et al. 2001; Nyman et al. 1986; Ratnaweera et al. 2015) and has been considered as that of typical polyelectrolytes in aqueous media (Helander et al. 2013). This has been relevant to our recent reports on the synthesis of supracolloidal lignin particles (Nypelö et al. 2015; Ago et al. 2016, 2017) and their interactions with proteins (Cusola et al. 2014; Fritz et al. 2015; Hoeger et al. 2012; Rahikainen et al. 2013; Salas et al. 2012). Here, dispersion interactions and hydrogen bonding, among others, affect the colloidal stability in aqueous dispersions. Aggregation is favorable if these effects are dominant; conversely, a stable colloidal suspension is afforded if strong repulsive electrostatic forces exist between the aggregates. For similar particles, van der Waals forces are attractive (Hubbe, Rojas 2008) and mostly independent of pH and ionic strength (Norgren et al. 2001). This is in contrast to the double layer electrostatic interactions which are repulsive (Hubbe, Rojas 2008) and highly dependent on these variables (Norgren et al. 2001). Therefore, to sum up, not only hydrogen bonding but also intermolecular van der Waals forces, non-bonded orbital interactions, hydrophobic interactions and ionic interactions are responsible for the self-association of lignin in solutions. At low pH, the charge of the lignin particles is low; therefore, it is expected that lignin association in solution results in flocculation. Nyman et al. (1986) found that in the absence of salt and high pH, lignin behaves as a stable colloid and only at high electrolyte concentration lignin flocculates due to decreasing thickness of the electrical double layer. Moreover, Norgren et al. (2001) studied the aggregation of softwood kraft lignin and concluded that pH, electrolyte concentration, the valence of the counterions and temperature are key parameters to regulate the interrelated effects. Norgren et al. (2002) studied the precipitation of kraft lignin in alkaline medium in the presence of various ions of the Hofmeister or lyotropic series and concluded that among the cations

studied, cesium, sodium, and potassium led to the lowest stability. Among the anions, chlorine and bromine were the least effective in enabling stability. These ion-specific interactions have been related to differences in adsorption/ desorption at interfaces and perturbations of water structuring (Norgren, Edlund 2003). In a salt-rich polyelectrolyte system, the electrostatic repulsion between the charged entities is strongly screened and this can be very unfavorable for the stability of the polyelectrolyte solution. Lignin precipitation can cause problems in given systems and re-dissolution may be possible by increasing the concentration of hydroxide ion; on the other hand, this can be detrimental in many industrial processes (Norgren et al. 2001). Conversely, surfactants can enhance the colloidal stability through a steric stabilization (Holmberg et al. 2002). Anionic surfactants, specifically bile acid salts, have been shown to endow colloidal stability of diluted KL solutions (Norgren, Edlund 2001) and were found to be effective in controlling aggregation. However, among the different types of surfactants, and compared to anionic ones, non-ionic amphiphilic molecules adsorb more strongly on hydrophobic surfaces due to the absence of electrostatic repulsion (Holmberg et al. 2002). Relatively little is known about the effects of non-ionic surfactant on the colloidal stability of kraft lignin solutions and understanding its colloidal aggregation is crucial as a prerequisite for successful control over aggregative phenomena and for improving its utilization, for example to use lignin as a filler or additive for polymer blends, interactions with proteins, lignin-derived functional materials, adhesives and foams. Therefore, the present study investigates the colloidal behavior of kraft lignins and unveils the effect of aqueous dispersion conditions, extensive also to respective submicron lignin particles and lignin in the so-called black liquors.

Materials and methods

Materials

The two main types of lignins were technical grades, namely, a softwood kraft lignin (SWK) donated by Domtar Inc. Plymouth Pulp Mill, NC (USA) and a hardwood kraft lignin (HWK) with high ash content donated by Suzano Pulp Mill (Brazil). Black liquor samples were obtained in our laboratory. The inorganic salts and surfactants were used without further purification.

Lignin characterization

The lignin samples were purified by washing with milliQ-water (Millipore) and centrifugation (Beckmann Centrifuge Model J-21C, 3000 rpm) several times in order to remove salts and other soluble components without affecting lignin. After the purification step, the lignin samples were freeze-dried prior to use. The insoluble and soluble components of the lignins were determined by a two step-acid hydrolysis procedure (Sluiter et al. 2008). The acid-insoluble lignin (Klason lignin) was determined gravimetrically, whereas the filtrate was used to determine acid-soluble lignin by UV-VIS spectroscopy at 205 nm (Lambda XLS, PerkinElmer,

Inc). After neutralization of this filtrate, sugar analyses were performed in a HPLC unit, as previously reported (Sluiter et al. 2008). Hydroxyl groups content and molecular weight determinations were carried out by ^{31}P -NMR and gel permeation chromatography (GPC) following procedures published elsewhere (Argyropoulos 1994; Granata, Argyropoulos 1995; Sadeghifar et al. 2012). Briefly, for ^{31}P -NMR a known amount of dried lignin sample was dissolved in a mixture of anhydrous pyridine/ CDCl_3 ; then endo-N-hydroxy-5-norbornene-2,3-dicarboximide solution was used as the internal standard and chromium (III) acetylacetonate in the above pyridine/ CDCl_3 solution was used as the relaxation reagent. Finally, phosphitylating reagent II (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added and the NMR spectra were acquired using a Bruker 300 MHz spectrometer. GPC measurements were performed on acetylated lignin samples using tetrahydrofuran as the eluent and polystyrene standards for calibration. The ash content was determined according to the TAPPI standard methods (TAPPI. 2002).

Preparation of lignin dispersions and colloidal characterization

The different lignin dispersions were prepared by dissolution in 10 mM NaOH under magnetic stirring for 3 h after which water was added to obtain the given lignin concentration. In given cases, the effect of electrolyte was tested by addition of 1 M NaCl. The dispersions were allowed to dissolve overnight. The pH was adjusted to 10.5, unless noted otherwise, with 1 M NaOH or 1 M HCl. During the experiments, the samples were incubated at 25 or 70°C in a temperature-controlled oven. The turbidity of the different aqueous dispersions was determined using an Orion AQ4500 turbidimeter at 25°C. The zeta potential of lignin dispersions and the apparent average size of aggregates were determined using a Zetasizer Nano-ZS (Malvern Instrument Ltd) at 25 or 70°C. The surface tension was measured using a DCA-312 Electrobalance from Cahn Instruments Inc. (Cerritos, CA, USA) equipped with a platinum Wilhelmy plate. Measurements were performed at 25 and 70°C using a thermostatic vessel connected to an external bath/circulator heating system.

Rheology

Rheological tests were performed in an AR2000 rheometer from TA Instruments (New Castle, DE, USA). The measurement system was equipped with a 40-mm-diameter parallel plate geometry. The apparent viscosity η (mPa) and shear stress (Pa) were recorded as a function of the shear rate $\dot{\gamma}$ from 1 to 200 s^{-1} using a 200 μm gap. Temperature was kept at 25°C, controlled by a Peltier heating system. Prior to test, the samples were equilibrated at 25°C for 2 min and an average of three repetitions is reported. The data was fitted to the Power-Law (Eq 1) (Ostwald 1925), Carreau-Yasuda (Eq 2) (Carreau 1972; Yasuda 1979), and Herschel-Bulkley (Eq 3) (Herschel, Bulkley 1926; Tang, Kalyon 2004) models:

$$\eta(\dot{\gamma}) = k\dot{\gamma}^{(n-1)} \quad [1]$$

$$\eta(\dot{\gamma}) = \eta_{\infty} + (\eta_0 - \eta_{\infty}) \left[1 + (\dot{\gamma} \lambda)^a \right]^{\frac{n-1}{a}} \quad [2]$$

$$\tau(\dot{\gamma}) = \tau_H + K_H^{(n)} \dot{\gamma}^n \quad [3]$$

where k is a consistency index and n is the flow behavior index. η_0 is the viscosity (mPa) at zero shear rate and η_{∞} is the viscosity (mPa) at infinite shear rate. λ corresponds to a constant with $1/\lambda$ the critical shear rate at which viscosity begins to decrease. a represents the width of the transition between η_0 and the power law region. K_H is the consistency coefficient (related to the strength of the structure). τ_H is the yield stress (Pa), which correlates with stability of the system and n is the flow index.

Stability and aggregation

Two systems were tested with regards to stability: lignin particles and lignin precipitated from black liquors (BL). The addition of calcium ions and non-ionic surfactant was studied for both systems. In the first case, SWK and HWK were used to produce lignin particles following the method of Lievonon et al. (2016) with a slight difference: here we utilized Spectra/Por Standard RC Dry Dialysis Tubing with 3.5 kDa molecular weight cut-off instead of the of 6-8 kDa (Spectrumlabs, USA). The aggregate size was monitored over time using dynamic light scattering (DLS, Malvern Zetasizer Nano ZS). In the second case, hardwood lignin was aggregated and precipitated from the respective BL. For this, white birch (*Betula papyrifera*) was digested (16% AA, 25% sulfidity, 160°C with 4:1 liquid-to-solid ratio) for an H-factor = 800 (kappa value of 20) and centrifuged to remove suspended solids. The turbidity of the BL samples was monitored by using an Orion AQ4500 turbidimeter. The lignin content was determined by UV-Vis spectrophotometer at 280 nm with an extinction coefficient of 20 l·g⁻¹·cm⁻¹ (Öhman et al. 2007). To determine the mass filtrated over time, a Whatman Nuclepore membrane (1 µm pore size) was used in a Millipore filtration unit operated at constant pressure (690 kPa). The experiments were conducted after the lignin samples were incubated in the respective BL that included salts and surfactant.

Results and discussion

The aggregation behavior of lignin in solution is affected by the nature of the lignin (its source) and the method used in its isolation. For instance, the kraft pulping process introduces phenolic hydroxyl and carboxyl groups in the lignin structure (Sjöström, 1989). The main characterization performed on the samples included phenolic hydroxyl groups, molecular weight and zeta potential (Table 1). Both samples exhibited similar phenolic content, which favors solubility in nonpolar solvents (Brown et al., 2000). However, the aliphatic hydroxyl content was lower in the case of HWK. The kraft lignins exhibit high negative values of zeta potential, which increases with the pH (Dong et al. 1996; Fritz et al. 2015). Related ionization mechanisms have been explained by a simplified model described by Dong et al. (1996) that includes the ionization of acid groups, especially the carboxylic groups that are added during pulping (Sjöström 1989). This could explain the similar

zeta potential values for the lignins studied. This observation is associated with the ionization of carboxyl and phenolic groups (Tang et al. 2015), as will be discussed later. The samples display a broad molecular weight distribution and a high polydispersity index (PDI), which is attributed to the isolation method used and the nature of the lignin sources (wood species). It is worth mentioning that residual bound carbohydrates may impact the colloidal stability and aggregation of the lignins. However, here we suggest a negligible contribution given the low values measured for this component (Table 1).

Temperature- and salt-induced aggregation.

The colloidal stability of lignin solutions is controlled by pH, ionic strength, molecular weight (Norgren et al. 2002), temperature (Norgren et al. 2001; Norgren et al. 2002), and lignin concentration (Sarkanen et al. 1984). These variables affect the turbidity of the colloidal dispersion, which reflects the state of the colloid, aggregation and also lignin swelling (Kontturi et al. 1990). An increase in temperature from 25 to 70°C promoted the aggregation of the lignins (Fig 1). For the softwood kraft lignin (SWK), there is a tendency to form aggregates even at room temperature, to an extent that is beyond the limit of the turbidity measurement (at 0.3% lignin concentration the turbidity was over the instrumental range). There is a threshold limit concentration (~0.3%) where temperature (70°C) promoted aggregation and finally caused precipitation of the lignin at pH 10.5. In the case of hardwood kraft lignin (HWK), there is a sharp increase in turbidity for concentrations above 0.20%, which is related to the formation of heat-induced aggregates.

According to the turbidity measurements shown in Fig 1b, the addition of 1 M NaCl affected the aggregation behavior of lignin samples. The turbidity values at 0.1% concentration significantly increased, especially for SWK (in this case the turbidity reached values beyond the instrumental range at 0.3% lignin concentration). A different behavior was reported by Nyman et al. (1986) who studied a high molecular weight kraft lignin from pine; it was proposed that the presence of a microgel core accounted for steric stabilization. In contrast, our results indicate electrostatic coagulation of lignin at pH 10.5 after addition of salt, suggesting the presence of bridging between adjacent particles. As expected, an increase in turbidity corresponded to an increase in size: for SWK the size values in the presence of NaCl 1 M increased from 1000 to 1500 nm; whereas for HWK sample the size range was larger, from ~500 to 2200 nm, indicating the differences between these two samples. Indeed, the magnitude of the zeta potential is reduced by the addition of mono- and multi-valent salts (but do not cause a shift in the IEP because of the negligible adsorption or affinity of Na⁺ or Ca²⁺ ions with lignin) (Dong et al., 1996). However, zinc sulfate and aluminum chloride cause charge reversal and a shift in IEP at high pH (Dong et al., 1996). The electrostatic repulsion between the charged units is strongly screened, and the ions can cause an increase in formation of intra- and intermolecular ionic

Table 1 – Chemical characterization of the different kraft lignin samples according to sugar analysis, lignin content, hydroxyl groups (³¹PNMR), molecular mass (GPC) and zeta potential.

Kraft lignin	Sugars %	Lignin ⁽¹⁾ %	Aliphatic OH mmol/g	Phenolic OH mmol/g	Total OH mmol/g	COOH mmol/g	Mw g/mol	PdI	ζ ⁽²⁾ , mV
SWK	<1	94 (5)	2.7	5.4	8.1	0.7	4,470	4.2	-37
HWK	1.2	85 (6)	1.8	5.1	6.9	0.5	3,240	3.2	-32

(1) Acid insoluble lignin % (Acid soluble lignin %); (2) Zeta potential measured on aqueous lignin solutions (0.1 wt%) at pH 10.5 and 25°C

Fig 1 – (a) Effect of lignin concentration and temperature on the lignin aggregation behavior in aqueous solution as monitored by turbidity (25 °C) after equilibration for 30 min at 70 °C. (b) The effect of electrolyte addition (1 M NaCl) on the aggregation behavior of the lignin solutions after equilibration at 70 °C for 30 min. The open symbols correspond to solutions containing lignin and NaCl. The samples included softwood kraft lignin (SWK) and hardwood kraft lignin (HWK). Note: An increase in turbidity is taken as indication of lignin aggregation in solution, provided no precipitation occurs. Note the breaks in the vertical axis for very large turbidity values

complexes with the counterion and act as a bridge between two or more charged groups on the lignin polyelectrolyte (Norgren et al., 2001). The aggregation kinetics was determined at various ionic strength as described in the section “Modes of aggregation and kinetics”.

Lignin association with surface active molecules

It can be anticipated that surfactants affect the aggregation behavior of lignin in solution and thus the colloidal stability of the system, particularly, via steric interactions (Holmberg et al. 2002; Lindström 1979). In order to assert the effect of different surfactant types, a screening study was carried out (data not shown), which revealed that non-ionic polyoxyethylene glycol sorbitan monooleate (denoted hereafter as “POE20”) increased the stability of the lignin dispersion, in the presence or absence of electrolytes. In contrast, a cationic surfactant (hexadecyltrimethylammonium bromide, CTAB) caused precipitation of lignin due to strong electrostatic interactions. The effect of nonionic surfactants can be rationalized by the fact that in absence of electrostatic repulsions they adsorb more strongly on hydrophobic sites (Holmberg et al. 2002) and could also partake in hydrophobic interactions with lignin (Eriksson et al. 2002). Therefore, the effect of the POE20 non-ionic surfactant on the dispersion behavior of lignin was further elucidated (Fig 2a, b). First, the dehydration and association of polyoxyethylene-type surfactants can be induced by heating and this effect, in principle, could be expected to interfere with the stabilization of the system.

However, our tests at high temperature in the presence of lignin indicated the opposite behavior: the equilibration of POE20 surfactant in the presence of lignin at high temperature (70°C, 30 min) was, in fact, effective in reducing the turbidity (turbidity values below 8 units, Fig 2a), indicating a better dispersion. Interestingly, the most notorious effect was found for SWK, where the turbidity decreased from 2800 to 2 units at 0.2% lignin concentration. These results were verified by measurement of the average size of the aggregates in aqueous media via dynamic light scattering (Fig 2c). The positive effect of surfactant in controlling aggregation could be explained by steric stabilization mechanisms, where the lignin molecules associate with the surfactant and reduce the unfavorable contact with water, thus stabilizing the system and maintaining them well dispersed under the given conditions.

Lignin association has been indicated to result in expanded “random coils” in alkaline media, which can adopt a rod-like conformation in the case of low molecular weight fractions. A more spherical shape has been suggested by lignin fractions of high molecular weight, as studied by size-exclusion chromatography (Sarkanen et al., 1982). In addition, it has been postulated that lignin can be considered as a fractal system, with guaiacyl units given chaotically branched fractal structures, while guaiacyl-syringyl units yield star-like

Fig 2 – The effect of non-ionic surfactant POE20 at 40 $\times$ cmc (red symbols) on the aggregation of (a) HWK and (b) SWK lignin aqueous solutions after equilibration (30 min at 70 $^{\circ}$ C) as measured by turbidity (Note the breaks in the vertical axis for very large turbidity values). (c) Dynamic light scattering (DLS) results for the apparent hydrodynamic diameter size. Note: surfactant concentration is given as multiple of the cmc (surfactant critical micelle concentration).

structures (Karmanov, Monakov 2003). This points to the fascinating but complex behavior of lignin in solution.

For the lignin samples studied, an increase in size was observed with increased concentration (neat lignin solution), due to the intermolecular interactions between neighboring molecules. For hardwood lignin (HWK), the addition of surfactant at concentrations above the critical micelle concentration (*cmc*) not only decreased the turbidity (Fig 2c) but also reduced the aggregate sizes, indicating a steric stabilization of the system. Presumably, the adsorbed surfactant prevents lignin association. Unfortunately, no good dynamic light scattering correlation from the cumulant method was obtained for SWK samples in the presence of surfactant, indicating a disorganized structure, which agrees with the drastic decrease in turbidity. Lindström (1979) studied the flocculation of kraft lignin solutions with a high molecular weight polyethylene oxide (POE), and concluded that the phenolic groups can act as the primary adsorption sites for this type of molecule. Such a hypothesis can be invoked to explain our observation for SWK and HWK, both having similar phenolic group content (Table 1).

Modes of aggregation and kinetics

So far, it is shown that kraft lignins aggregate over time, especially in the presence of salt, whereas the addition of a non-ionic surfactant reduces aggregation and brings about a colloidal stabilizing effect. The kinetics of aggregation was studied at various ionic strengths using a low lignin concentration (0.1%) and the stability ratio (*W*-ratio) was calculated from the slope of the turbidity plots (Fig S1). The dimensionless *W*-ratio (Hogg et al. 1966) factors the aggregation rate coefficient in the fast regime, and that at the conditions of interest. Thus, it represents the ratio of rapid or diffusion-controlled aggregation (in the absence of repulsive forces) to the slow aggregation. The stability ratio is close to unity in the fast regime, increases in the slow regime, and becomes very large when the suspension is stable. Therefore, with increasing repulsion the value of *W* increases. At high ionic strength, aggregation is promoted as revealed by the high turbidity values for the lignin samples. From the turbidity plots, there is a sharp change

Fig 3 – Stability ratio W based on turbidity measurements of aqueous colloidal dispersions of lignins (a) in the absence and in the (b) presence of non-ionic surfactant (POE20 at $6 \times \text{cmc}$). The profiles are plotted as a function of NaCl concentration at pH 10.5 and 70°C .

in slope at high NaCl concentration and, in the interval between 1.2–1.5 M, the curves overlap. This region can be recognized as a rapid aggregation or diffusion-limited aggregation, whereas at salt concentrations below 1.0 M the behavior corresponds to a slow regime. Based on this observation, the W -ratio was determined and presented in Fig 3. Regions of significant colloidal stability ($W \gg 1$), low stability ($W > 1$), and instability ($W \approx 1$) are clearly observed. In all the cases, the critical coagulation concentration (ccc), which separates the fast from the slow regime, was located at an electrolyte concentration of ~ 1.2 M NaCl, which is in agreement with another study (Norgren et al. 2002). Interestingly, at NaCl concentrations from 0.5 to 1 M, the stability curve shows a change in the slope. Higher slopes were observed in the presence of the non-ionic surfactant, especially for HWK lignin where, for example, the addition of surfactant improved the stability at low electrolyte concentration (< 0.8 M NaCl). The presence of a simple electrolyte induces a reduction of the electrostatic double layer thickness, whereas it has been hypothesized that polyethylene oxide forms interparticle bridging. Thus, from other studies, it was expected that the electrostatic repulsion should decrease at smaller interparticle distances and consequently the amount of electrolyte needed to cause flocculation was expected to be less than in the absence of the polymer (Lindström 1979). However, such behavior was not observed at this point, suggesting that no bridging occurred; therefore, the addition of non-ionic surfactant ($6 \times \text{cmc}$) mainly caused steric stabilization.

The stability of lignin solutions also depends on its chemical and physical heterogeneity (Norgren et al. 2002). An experiment was performed to test the ability of a salt/surfactant system to flocculate and precipitate the lignins instead of maintaining the colloidal stability. For this, the stability of the low molecular weight HWK lignin was tested for turbidity over 48 h at different sodium chloride and non-ionic surfactant concentrations, as shown in Fig S2. At 0.1% HWK lignin concentration all conditions induced aggregation up to certain level; at

the highest salt and surfactant concentrations the lignin precipitated out after 48 h. A somewhat different behavior was observed at a slightly higher lignin concentration, 0.3%, where aggregation was faster and more extensive even after 30 min equilibration. In this case, lignin started to precipitate at 0.8 M NaCl and POE20 $6 \times \text{cmc}$. Thus, bridging flocculation by the non-ionic surfactant at high concentration seems to favor the precipitation of lignin in the system, probably as a result of the reduced electrical double layer that decreases the inter-particle distance. Overall, it is concluded that the addition of the non-ionic surfactant improves the stability of the systems up to certain level; then, a synergistic effect with salt promotes aggregation and precipitation. These results revealed the possibility to use a mixture of salt and nonionic surfactant to recover lignin from wastewater and from black liquors, as it is presented in the respective section.

Rheology

Since most of the samples experienced aggregation in a relatively short period, it was of interest to evaluate the aggregation behavior through viscosity measurements of samples equilibrated at 70°C for 30 min. The plots of apparent viscosity as a function of the shear rate for HWK and SWK are shown in Fig 4. It is clear that the apparent viscosity decreases as the shear rate increases, indicating a shear thinning behavior for all salt concentrations. As the lignin concentration increased and after 30 min at 70°C , the viscosity increased. A possible explanation is that with no equilibration time the formed clusters (if any) become more compact and the viscosity is lowered. Lindström (1979) concluded that heating causes intramolecular lignin chain rearrangements in alkaline solution due to disruption of hydrogen bonds. As temperature and time increases, these clusters come into contact, creating larger aggregates and leading to an increased viscosity (aggregate immobilization). The difference in the total hydroxyl group content may explain the difference in viscosity for the two lignin samples. Moreover, in the absence of electrolytes, or

without a counter-ion, the negative charges produce strong intermolecular repulsion and thus a more expanded molecule. This may also explain the high viscosity of lignin without salt/surfactant as the lignin content increases, which was revealed by the viscosity at zero shear rate obtained by fitting the data to the Carreau-Yasuda model (Table S1, S2). Besides, addition of

electrolyte (NaCl) to the solutions decreases the extent of the electrical double layer around lignin. The three different models used to fit the data, Power-Law, Carreau-Yasuda, and Herschel-Bulkley, yielded the parameters and correlation coefficients given in Table S1, S2.

Fig 4 – Apparent viscosity (profiles on the left) and shear stress (profiles on the right) for the different alkaline lignin solutions as a function of shear rate in the absence (open circles) and in the presence of 1 M sodium chloride (solid circles). The case where non-ionic surfactant (40×cmc) is added is also shown (triangle symbols). Viscosity and shear stress plots for hardwood kraft (HWK) are shown in (a) and (b) and for softwood kraft (SWK) in (c) and (d), respectively.

Fig 5 – Zero-shear viscosity η_0 of hardwood kraft (HWK) and softwood kraft (SWK) lignin solutions as a function of the volume fraction. The data was fitted to the power law equation reduced to $y=ax^b$, and the values for a , b , and R^2 were 3.2, 0.4 and 0.99; 10.9, 0.54, and 0.92 for HWK in water and saline solutions, respectively. Attempts to fit SWK data yielded poor results.

Power law and Carreau-Yasuda models help to explain the zero-shear viscosity. In general, the viscosity at zero-shear rate of HWK increased by the addition of salt (*Table S1*), whereas for SWK it decreased (*Table S2*) as the lignin content increased. However, compared with the effect of temperature, the addition of salt reduced the viscosity at zero shear rate, probably due to fact that the addition of cations reduces repulsion and molecular expansion, thus decreasing network structure. The non-ionic surfactant decreased the viscosity in all cases, possibly due to the steric stabilization of the lignin

Fig 4 shows the shear stress as a function of shear rates (right frames). It can be seen that above 15 s^{-1} , the shear stress exhibits a yield value and undergoes a linear increase that is explained by the Herschel-Bulkley model. This model predicts a higher apparent viscosity when K_H is higher, which means the system has a strong structure upon shear. On the other hand, τ_H (yield stress) explains the stability of the system, the higher the value, the stronger the stability of the system. The presence of salt and non-ionic surfactant affects the organizational structure of the aggregates at low shear rates by decreasing the shear stress, which would indicate a more organized structure. The higher K_H and τ_H values were obtained for the HWK lignin, suggesting a strong and compact structure, in agreement with the high viscosity and well-defined sizes (*Fig 2*).

From the Carreau-Yasuda model, the zero-shear viscosity was determined and plotted against the volume fraction in order to better display the concentration dependence, as shown in *Fig 5*. Data for lignin concentrations higher than 0.3 wt% are not presented because of precipitation. The data was fitted to a power-law equation but attempts to fit the data for SWK gave unreasonable values. The exponent value for HWK lignin in water was 0.38. In salt (1 M NaCl), this value was 0.54, indicating a denser HWK packing in saline solutions. No good fitting was observed for systems containing non-ionic surfactant and lignin, suggesting that aggregation was prevented due to steric stabilization. The above results coincide with the trend of decreasing surface tension at the water-air interface, as shown in *Fig S3*. Low surface tension is a desired property in several applications where lignin can be used, such as in, among others, emulsions (Nypelö et al. 2015; Ogunkoya et al. 2015), spinning (Ago et al. 2012), and carbon fibers (Oroumei et al. 2015). Lignin can be considered as a surface-active macromolecule in aqueous media since it reduces the surface tension, depending on the conditions (Rojas et al., 2007). All the samples exhibited surface tension values lower than water and decreased with the increased lignin concentration. It has been suggested that the increased hydrophilic groups of lignin decrease its surface activity and increase its solubility (Matsushita et al., 2008). The lowest surface tension was found for samples containing the non-ionic surfactant even after the solution was cooled down at room temperature (30 mN/m for POE20 solution at $40\times cmc$). In the case of saline solutions at 70°C , NaCl affects aggregation, which might explain the similar values of surface activity for the aqueous and saline lignin solutions, due to the ability of ions to cause

perturbations in water structure (Norgren, Edlund 2003). No correlation was found between the surface tension of the solutions and the molecular weight of lignin.

Relevance of colloidal stability and aggregation

The colloidal behavior of lignin in solution is not only of great importance from an environmental viewpoint, for example, in wastewater treatment, but in many other areas. Moreover, lignin aggregation significantly impacts the development and preparation of advanced materials. In order to further inquire into this subject, the stability of lignin nanoparticles (prepared by the method developed by Lievonen et al. 2016) and black liquor was tested by addition of salt and non-ionic surfactant. The surface charge provided by phenolic hydroxyl and carboxylic groups on lignin is expected to facilitate the electrostatic double layer, which favors (nano)particle stabilization but it can be challenged by addition of salt and surfactants. For this, the stability of submicron lignin particles was studied and the particle size over a period of 10 days is shown in *Fig 6*. In pure water, the initial average size (day 0) was ~ 285 and ~ 460 nm for SWK and HWK, respectively. The initial zeta potential values of the lignin particles were ~ -60 , and ~ -49 mV for HWK, SWK, respectively. Similar values have been reported previously (Lievonen et al. 2016). The surface potential of lignin in solution can be affected by pH since the thickness of the electrostatic double layer decreases at low values; however, pH was found to have a minor effect on the tested submicron lignin particles dispersed in water. This may indicate that the carboxylic and phenolic groups play a minor role in aggregation of these particles. Different particle aggregation behavior was found by the addition of salt. Aggregation was observed upon increasing NaCl concentration from 0.5 to 1 M. The most stable system was SWK at 0.5 M NaCl, with no significant changes in particle size after 10 days at pH 10.5. HWK particles were the most affected since no reliable data was collected from the size measurements, indicating the presence of large or not well-defined aggregates under the presence of salt. These results agree with the DLVO theory (Derjaguin, Landau 1941; Verwey et al., 1948) that predicts a decrease in the double layer repulsion between particles upon salt addition, thus aggregation is promoted as the van der Waals forces become dominant. Interestingly, lignin particles carrying the non-ionic surfactant maintained their stability and size, a verification that particle aggregation did not occur. The concentration of the non-ionic surfactant seems to have a minor effect on the average particle size. The steric stabilization provided by the surfactant may be useful in lignin applications as a colloid.

In order to examine the effects of salt and surfactant on the stability of industrial streams and the potential for lignin isolation, a black liquor was tested under similar conditions as those used in the particle systems. After some investigations to determine the appropriate conditions for aggregation (*Fig S4*), the results of mass filtered over time are shown in *Fig 7*. It is worth mentioning that filtration of neat black liquor sample was faster (completed in less than 50 s) compared to the other conditions studied and no cake was formed on the

Fig 6 – Stability of lignin particles at room temperature monitored by their average apparent size (dynamic light scattering) in water, electrolyte and surfactant solutions at two pH levels: 10.5 (profiles on the right) and 7 (profiles on the left). Sodium chloride was used at 0.5 and 1 M. Surfactant (POE20) was used at a concentration close to the cmc (=cmc) and at higher concentrations ($40\times$ cmc or >cmc, as noted). Initial lignin concentration 10 mg/ml. Note that for HWK the addition of salt affected the aggregate shape and no reliable data was obtained from DLS analysis.

Fig 7 – Mass of lignin from hardwood black liquor (BL) (~14g/L lignin), retained on a Fann filter paper (47 mm diameter, 1 μm pore size) as a function of time in the presence of salt or surfactant: BL + POE20 2g/L (up triangle), BL + Ca²⁺, 4g/l (circle), BL + POE20, 0.6g/l + Ca²⁺, 4g/l (square), and BL + POE20, 2g/l + Ca²⁺, 4g/l (down triangle). In all the cases, the pH was 12. The photos shown as inset correspond to the residual lignin deposited over the Fann filter paper after 14 ml BL dispersion was processed at constant pressure (~690 kPa) and room temperature. Note that in the presence of non-ionic surfactant no lignin cake was formed.

filtration membrane surface. Similar results were obtained for black liquor equilibrated with non-ionic surfactant at 2 g/l. In contrast, the synergistic effect of salt (Ca^{2+} ions) and surfactant promoted colloid aggregation to a greater extent than calcium ions, leading to the formation of a lignin cake upon filtration at high lignin concentration in alkaline conditions. Usually, precipitation of lignin is carried out by acidification (Zhu, Theliander 2015) and ultrafiltration (Helander et al. 2013; Jönsson et al. 2008). Therefore, these results may bring new opportunities to separate and fractionate lignin from process streams avoiding environmental and corrosive problems due to the decrease in pH value, as well as facilitating filtration steps by increasing aggregate size. However, further studies are needed to investigate the properties and purity of the precipitated lignin as well as to optimize conditions to achieve a maximum lignin recovery yield

Conclusions

The colloidal aggregation of kraft lignins was studied by evaluation of turbidity, dynamic light scattering, and rheology. Lignin tended to self-aggregate over time, especially at high temperatures (70°C). On the other hand, the presence of a non-ionic surfactant improved lignin colloidal stability due to steric stabilization effects. Sodium chloride induces fast aggregation of kraft lignins derived from hardwoods and softwoods (HWK and SWK). According to the results, salt screens the electrostatic repulsions, causing the formation of intra and inter molecular complexes. Rheology measurements indicate a disruptive effect by electrolytes involving the swelling of the aggregates and the weakening of their structure. By taking advantage of aggregation, the filtration of hardwood black liquor is improved, whereas colloidal stability is achieved for lignin particles.

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Supporting Information

This supporting information comprises four figures and two tables; the effect of different surfactants on aggregation monitored by turbidity (*Fig S1, S2*); the effect of salt and non-ionic surfactant on surface tension (*Fig S3*); end-turbidity values for black liquor samples incubated with salt and non-ionic surfactant (*Fig S4*), and the fitted parameters for rheology models (*Tables S1, S2*)

Fig S1 – Turbidity of lignin solutions as a function of time at various NaCl concentrations and non-ionic surfactant (POE20 at $6\times\text{cmc}$) at pH 10.5 and 70°C. Aggregation was significant for (A, B) HWK and (C, D) SWK samples. The rate of aggregation was calculated from the slope between 30 to 120 min

Fig S2 – Turbidity measurements of HWK lignin as a function of time, sodium chloride and surfactant concentrations at pH 10.5 and 70 °C. Two lignin concentrations, 0.1% (left) and 0.3% (right), were studied in order to highlight differences in aggregation behavior. In (a) the systems aggregated over time and lignin precipitated at 0.5M NaCl + 40×cmc, 0.75M NaCl + 40×cmc, 1M NaCl + 6×cmc, and 1M NaCl + 40×cmc conditions, as observed by naked eye. In contrast, most of the systems shown in (b) are aggregated or the aggregation extent was higher than that in (a) and lignin precipitation occurred at 0.5M NaCl + 40×cmc, 0.75M NaCl + 6×cmc, 0.75M NaCl + 40×cmc, 1M NaCl + 6×cmc, and 1M NaCl + 40×cmc, as observed by naked eye and the rapid decrease in turbidity values. Note the broken turbidity axis at 100 (a) and 9000 (b) turbidity units.

Fig S3 – Effect of electrolyte and surfactant on surface tension of the different lignin aqueous solutions after incubation for 30 min at 70 °C. The open symbols correspond to the surface tension measured after cooling down at 25 °C, whereas the closed symbols are the values determined at 70 °C.

Fig S4 – Final turbidity of black liquor samples after equilibration (24 h at 70 °C) in the presence of different salts and non-ionic surfactant concentrations: POE20 (up triangle), NaCl (down triangle), Ca²⁺ (open circle), and a mixture of POE and Ca²⁺ (solid circle). A control sample was included (square). The concentrations used are shown in the plot. The pH was kept at 12.

Table S1 – Fitted parameters for given rheology models for HWK lignin solutions at different lignin concentrations (%), with and without the addition of sodium chloride and a non-ionic surfactant, T80 (40 × cmc).

%wt	Power law				Carreau-Yasuda					Herschel-Bulkley			
	<i>k</i>	<i>n</i>	<i>R</i> ²		<i>n</i>	<i>a</i>	η_0	λ	<i>R</i> ²	τ_H	<i>K_H</i>	<i>n</i>	<i>R</i> ²
0.05	25 °C	24.9±6	0.4±0	0.978	0.0±0	46.2±3	176.4±13	4.8±3	0.984	0.0444±0.04	0.0022±0.00	0.9±1	0.999
	70 °C	62.8±9	0.2±0	0.971	0.1±0	82.1±2	156.4±14	2.2±0	0.997	0.0043±0.00	0.0078±0.01	0.5±1	0.995
	+NaCl	46.7±12	0.0±0	0.998	0.0±0	36.5±7	132.4±5	3.6±1	0.983	0.0263±0.03	0.0002±0.00	1.2±1	0.999
	+T80	16.2±0	0.0±0	1.000	0.0±0	40.4±0	94.1±6	12.2±0	0.926	0.0024±0.00	0.0007±0.00	1.0±1	1.000
0.1	25 °C	133.7±0	0.0±0	1.000	0.0±0	43.5±0	253.7±0	1.8±0	0.990	0.0000±0.00	0.0358±0.00	0.4±0	0.987
	70 °C	110.1±7	0.1±0	0.998	0.2±0	35.4±2	204.6±10	3.3±0	0.988	0.0091±0.01	0.0526±0.03	0.5±0	0.987
	+NaCl	74.3±21	0.0±0	0.999	0.0±0	11.0±0	257.0±38	4.2±1	0.998	0.0402±0.02	0.0004±0.00	1.2±0	0.999
	+T80	14.6±1	0.0±0	1.000	0.0±0	20.2±0	74.7±5	10.5±2	0.929	0.0039±0.00	0.0006±0.00	1.1±0	1.000
0.2	25 °C	176.3±43	0.2±0	1.000	0.2±0	34.7±8	318.2±69	2.1±0	0.996	0.0304±0.03	0.1963±0.03	0.2±0	0.987
	70 °C	162.2±17	0.2±0	0.983	0.2±0	34.3±1	266.4±14	1.9±1	0.987	0.1530±0.15	0.1175±0.10	0.3±0	0.945
	+NaCl	91.3±25	0.0±0	0.988	0.0±0	13.3±1	227.9±57	3.5±1	0.987	0.0656±0.03	0.0010±0.00	1.0±0	1.000
	+T80	14.2±5	0.0±0	1.000	0.0±0	6.8±2	66.9±3	8.4±0	0.628	0.0040±0.00	0.0007±0.00	1.0±0	1.000
0.3	25 °C												
	70 °C												
	+NaCl	188.8±39	0.0±0	0.999	0.0±0	22.0±0	407.5±30	2.0±0	0.999	0.1492±0.02	0.0012±0.00	0.9±0	0.999
	+T80	14.7±1	0.0±0	1.000	0.0±0	21.7±2	87.3±4	11.6±0	0.927	0.0023±0.00	0.0009±0.00	1.0±0	1.000

Table S2 – Fitted parameters for given rheology models for SWK lignin solutions at different lignin concentrations (%), with and without the addition of sodium chloride and a non-ionic surfactant, T80 (40 × cmc)

%wt	Power law				Carreau-Yasuda					Herschel-Bulkley			
	<i>m</i>	<i>n</i>	<i>R</i> ²		<i>n</i>	<i>a</i>	η_0	λ	<i>R</i> ²	τ_H	<i>K_H</i>	<i>n</i>	<i>R</i> ²
0.05	25 °C												
	70 °C	107.8±23	0.1±0	0.987	0.1±0	53.3±1	195.0±0	2.3±0	0.973	0.0371±0.04	0.022±0.02	0.5±1	0.997
	+NaCl	40.4±9	0.0±0	0.973	0.0±0	59.6±8	92.1±15	3.6±0	0.914	0.0194±0.02	0.001±0.00	1.0±1	0.999
	+T80	30.9±10	0.1±0	0.935	0.0±0	44.2±0	69.4±4	4.1±1	0.933	0.0130±0.01	0.000±0.00	1.2±1	0.996
0.1	25 °C	160.3±25	0.0±0	0.994	0.0±0	34.6±3	229.4±12	2.6±0	0.996	0.0463±0.00	0.002±0.00	0.9±0	0.996
	70 °C	31.6±16	0.1±0	0.993	0.0±0	45.1±5	192.7±3	6.9±2	0.987	0.0132±0.01	0.006±0.00	0.7±0	0.999
	+NaCl	26.9±2	0.1±0	0.951	0.0±0	56.8±10	87.1±4	3.7±0	0.950	0.0043±0.00	0.005±0.00	0.8±0	0.999
	+T80	20.7±1	0.0±0	0.940	0.0±0	42.7±2	46.9±5	5.8±0	0.964	0.0064±0.00	0.000±0.00	1.1±0	0.999
0.2	25 °C	142.1±47	0.0±0	0.996	0.0±0	30.4±3	291.1±49	2.8±0	0.990	0.0568±0.03	0.003±0.00	0.8±0	0.994
	70 °C	31.3±1	0.1±0	0.981	0.1±0	45.1±5	184.7±2	9.9±3	0.981	0.0167±0.01	0.003±0.00	0.8±0	0.999
	+NaCl	16.3±4	0.1±0	0.996	0.0±0	56.8±10	45.5±1	5.0±1	0.884	0.0024±0.00	0.000±0.00	0.0±0	1.000
	+T80	10.2±1	0.3±0	0.959	0.0±0	44.2±0	63.6±11	5.5±0	0.969	0.0104±0.01	0.001±0.00	1.1±0	0.999
0.3	25 °C	115.6±39	0.0±0	0.971	0.0±0	31.9±0	263.0±31	3.4±1	0.979	0.0868±0.09	0.001±0.00	1.1±1	0.997
	70 °C	35.9±8	0.1±0	0.989	0.0±0	45.7±4	203.1±23	8.8±2	0.996	0.0056±0.01	0.004±0.00	0.8±1	0.999
	+NaCl	18.5±3	0.0±0	0.983	0.0±0	48.6±19	51.6±3	4.8±0	0.951	0.0107±0.01	0.001±0.00	1.1±1	0.999
	+T80												