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# Sulfate and Surfactants as Boosters of Kraft Lignin Precipitation

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In the spirit of the biorefinery concept, an increasing interest in further utilization of technical lignins outside the pulp mills has arisen. In this context optimization of the precipitation process to increase the yield of the lignin recovered is of great importance. The objectives of this investigation have been to study how specific salts and surfactants affect kraft lignin yield during precipitation and washing. From the results it was seen that additions of sodium sulfate increased the yield of precipitation at elevated temperatures at much lower concentrations than sodium chloride. Earlier studies of the effect of monovalent salts on kraft lignin stability have shown that specific ions either increase or decrease the formation of precipitates during kraft lignin aggregation. Thus, the presented results in this study further strengthen this dependency concerning divalent anions. Regarding the role of surfactants as precipitation enhancers, cationic surfactants gave rise to fast aggregation and relatively high yields. This was found mainly due to attractive electrostatic interactions between the cationic surfactant headgroup and the oppositely charged groups on the kraft lignin macromolecules, introducing an increased degree of hydrophobicity of the lignin and thus a decreased stability. The nonionic surfactants tested affected the system very differently. In some cases the aggregation was fast and the aggregates became relatively large before settling, whereas some surfactants induced the formation of relatively dense precipitates that settled rapidly. Concerning kraft lignin precipitate washing, calcium chloride at concentrations in the millimolar region decreased the lignin losses dramatically.

## Introduction

Within the research program FRAM (future resource-adapted pulp mill), one of the goals has been to remove the kraft lignin (KL) excess that will exist if the pulp production capacity is increased at the pulp mill without investments in the recovery system.<sup>1</sup> After isolation, the lignin product would be used as a biofuel in power plants far away from the pulp mills, or in the most advantageous case, further be processed to yield new products. Improvements of the isolation procedure include better separation and decreased losses during washing of the precipitated lignin and thereby better yields, and require a better understanding of the KL aggregation process.

After cellulose, lignin is considered to be the most abundant biopolymer. The chemical structure of lignin can be somewhat difficult to define. The lignin polymers are based on a phenylpropanoic skeleton, with coniferyl, sinapyl, and *p*-coumaryl alcohol as the base units. Among these, softwoods contain predominantly coniferyl alcohol, whereas mostly sinapyl and *p*-coumaryl alcohol are found in hardwoods and grasses. The monolignols are linked together through about 10 different chemical bonds and this finally leads to lignins' amorphous and irregular macromolecular structures.<sup>2</sup> Indeed, the ways in which the units are linked are found partly species-dependent, and matters further complicating accurate elucidations of native lignins are the introduction of changes in the chemical structure due to the different protocols in which lignin may be extracted and isolated.

Regarding lignin dissolved in the digester during kraft cooking, it has been shown that in the presence of high concentrations of monovalent metal ion salts at slightly alkaline pH conditions, the KL starts to aggregate into large clusters, which finally precipitate.<sup>3</sup> When lignin is precipitated, the kinetics of aggregation can generally be referred to one of two

well-defined limiting regimes; the rapid diffusion limited cluster(colloid)–cluster(colloid) aggregation (DLCA) and the slow reaction-limited cluster(colloid)–cluster(colloid) aggregation (RLCA).<sup>4</sup> DLCA is the result of negligible repulsive forces between colloidal particles and in RLCA the sticking probability is much lower due to the existence of repulsive forces between the particles.<sup>5</sup> Several collisions between particles are possible before aggregation. The RLCA-aggregates are relatively compact, denser than the DLCA-aggregates, and the fractal dimensions are higher. Analysis of mass fractal dimensions has shown to be a good discriminator in distinguishing between different aggregation processes.<sup>6</sup> A great deal of the understanding of aggregation phenomena has been adopted from the DLVO-theory. The onset (nucleation) of aggregation is very important for the final aggregate structures, especially during DLCA.

At certain solution conditions the KL fragments start to self-associate into colloidal particles (nucleation). The particles grow both in number and size and finally fractal KL cluster structures are formed.<sup>4</sup> It has been shown earlier that the self-aggregation of KL solutions is differently affected by ions belonging to the so-called Hofmeister series.<sup>7</sup> Increased precipitation induced by inorganic anions is especially notable since a general electrostatic approach to explain the phenomenon is lacking.<sup>7–9</sup> Among tested monovalent cations, cesium ions induce the lowest KL stability, and in the case of monovalent inorganic anions, chloride ions give the lowest KL stability.<sup>7</sup>

Concerning surface-active agents, surfactants, bile salts have been shown to stabilize KL solutions against precipitation.<sup>10</sup> However, indications of that other surfactants have destabilizing effects on KL solutions were also shown.

An efficient recovery of lignin based on precipitation is a prerequisite for the success of using lignin outside the mill. Thereby, the objective of this work has been to investigate how the lignin aggregation and precipitation is affected after additions of different inorganic salts and surfactants. The yield of

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**Table 1. List of Surfactants That Have Been Used in This Investigation**

| surfactant | charge <sup>a</sup> | chemical compound                  | HLB <sup>b</sup> | technical use                  | supplier                 | purity |
|------------|---------------------|------------------------------------|------------------|--------------------------------|--------------------------|--------|
| AG6210     | n                   | alkylglucoside                     | -                | dispersant, wetting agent      | Akzo Nobel               | ~60%   |
| Berol 02   | n                   | nonylphenol ethoxylate             | 10.9             | emulgator                      | Akzo Nobel               | 100%   |
| Berol 296  | n                   | nonylphenol ethoxylate             | 15.2             | emulgator                      | Akzo Nobel               | 100%   |
| Brij 35    | n                   | POE(23)lauryl ether                | 16.9             | detergent in HPLC applications | Merck-Schuchardt         | ~97%   |
| Brij 56    | n                   | POE(10)cetyl ether                 | 12.9             | emulsifier                     | Sigma-Aldrich            | ~97%   |
| Brij 58P   | n                   | POE(20)cetyl ether                 | 15.7             | emulsifier                     | Fluka                    | ~97%   |
| Brij 96V   | n                   | POE(10)oleyl ether                 | 12.4             | emulsifier                     | Fluka                    | ~97%   |
| DoAB       | c                   | dodecylammonium bromide            | -                | dispersant, emulsifier         | synthesized <sup>d</sup> | >99%   |
| DoBS       | a                   | dodecylbenzene sulfonic acid       | -                | detergent                      | Sigma-Aldrich            | ~80%   |
| DoPyB      | c                   | 1-dodecylpyridinium bromide        | -                | research                       | synthesized <sup>d</sup> | >99%   |
| DoTAC      | c                   | dodecyltrimethyl-ammonium chloride | -                | chemical intermediate          | Fluka                    | >99%   |

<sup>a</sup> Notations: a (anionic), c (cationic), n (nonionic). <sup>b</sup> HLB; Hydrophile-Lipophile Balance, data from the supplier. <sup>c</sup> POE; polyoxyethylene. <sup>d</sup> Synthesized at Mid Sweden University.

precipitation and the aggregation kinetics have been focused. The stability of KL precipitates during washing has also been studied.

## Experimental Section

**Materials.** Two different types of softwood kraft lignins have been used in this work, Indulin AT and Curan 100. Indulin AT (lot 123H0189) was supplied by Sigma-Aldrich and Curan 100 was a kind gift from Borregaard Lignotech, Sweden. The inorganic salts used (p.a. quality) were supplied by Merck or Riedel-deHaën.

The data of the surfactants used are listed in Table 1.

It should be noted that surfactants in the Brij-series have very different numbers of oxyethylene (ethoxy) groups and a great variation in the number of carbons in the hydrocarbon chains. The head groups of ethoxylated surfactants are also much larger than for many other surfactants. Berol 02 and Berol 296 also have oxyethylene head groups, but a phenyl group is incorporated between the hydrocarbon chain and the oligomeric oxyethylene groups.

**Stock Solution Preparation.** Solutions of Curan 100 or Indulin AT were prepared to concentrations of approximately 10 g L<sup>-1</sup>. Indulin AT was used in some of the experiments as a reference. The lignin was allowed to dissolve in 30 mL of 1.0 M NaOH for 3 h and thereafter gently diluted with small portions of Milli-Q water during several hours. The solution pH was lowered to 10.5 by careful additions of 0.1 M HCl. Samples of the stock solution were transferred to other vessels and additions of salts and surfactants were done. When salt was added to the solution, generally the pH-value decreased slightly and was readjusted to 10.5 with 0.1 M NaOH.

**Methods. Turbidity Measurements.** A Hach RATIO/XR 43900 turbidimeter equipped with a tungsten lamp was used. The sample solution was transferred to cuvettes, measured before heating, and placed into a water bath of 75 °C. During the heating several turbidity measurements were performed at specific times.

**pH-Measurements.** A Mettler Delta 340 pH-meter was used. The electrode was a Mettler Toledo with pH and temperature ranges between 0 and 14 and 0 and 100 °C, respectively. The electrode was calibrated by buffer solutions at two different pH values; 7.00 and 12.00. The pH-measurements were performed at 20 °C.

**Lignin Yield Determination.** A Shimadzu spectrophotometer, UV-160A, was used in the UV-measurements. A calibration curve of Curan 100 was obtained from measurements of eight samples of Curan 100 diluted in 0.1 M NaOH to different concentrations at 280 nm. The absorption coefficient for Curan 100 was determined to 20.75 L g<sup>-1</sup> cm<sup>-1</sup>.

After precipitation, the samples were centrifuged in a Beckham J2-HS centrifuge at 3000g for 15 min and the absorbencies of supernatant solutions were measured. The samples were diluted with 0.1 M NaOH to an absorbency range of 0.1–1.0 to ensure accurate determinations with respect to the Beer–Lambert correlation rule between absorbance and concentration. The pH of the analyzed samples was always above 12.6 and the degree of dissociation of phenolic groups in the kraft lignin was thus close to 1 at the ambient temperature.<sup>11</sup> The yields of precipitation of the different samples were calculated from the ratio between the corresponding supernatant concentration and the stock solution concentration. It was checked for that the surfactants used in the experiments did not give any significant contribution to the absorbency at prevailing concentrations.

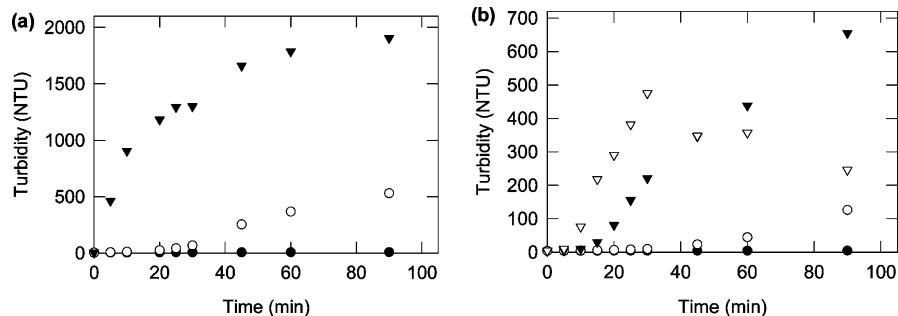
**NMR Self-Diffusion Measurements.** Proton nuclear magnetic resonance (NMR) self-diffusion measurements were performed at 25 °C on a Bruker DPX 250 MHz spectrometer applying pulsed field gradients. From the measurements of the Curan 100 and Indulin AT samples dissolved in 0.1 M NaOD a log-normal distribution function of the self-diffusion coefficients, often applied in evaluations of polymer samples,<sup>12–14</sup> was found to fit the obtained NMR data very well.

**Precipitate Washing.** The precipitates (~2 g) were transferred to the washing liquor (~167 mL) and washed under rigorous stirring during 10 min. Separation of solid and dissolved material was then obtained by centrifugation as described earlier. This procedure was repeated three times for each sample and the supernatants were collected together and analyzed by UV-spectrophotometry to determine the lignin loss. Washing liquors containing different amounts of inorganic salts and one of the surfactants were used in the experiments.

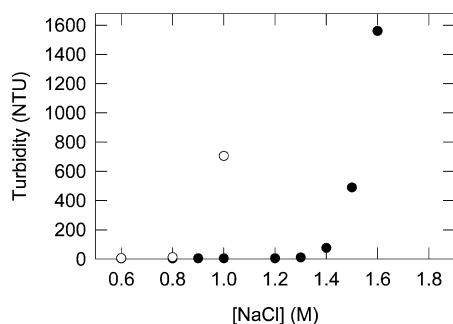
## Results and Discussion

**Salt Effects.** The kinetics of self-aggregation and precipitation of KL at a certain alkalinity has been shown earlier to be dependent on the ionic strength and the temperature.<sup>3,4</sup> In Figure 1a it can be seen that Indulin AT immediately starts to precipitate at a concentration of 1.0 M NaCl, whereas it is shown in Figure 1b that Curan 100 is completely stable at this salt concentration. Increase in turbidity due to self-aggregation is noticed at 1.2 M NaCl after 45 min and after 15 min at 1.3 M. At a concentration of 1.4 M NaCl, self-aggregation begins after 10 min in the Curan 100 solution and the turbidity values decrease again after 45 min due to precipitate settling.

Figure 2 shows the turbidity values for Curan 100 and Indulin AT after 10 min heating at 75 °C. These results should be compared with the results shown in Figures 1a,b. At a concentration of 1.0 M NaCl, Indulin AT starts to precipitate after 10 min. On the other hand, the Curan 100 solution demands



**Figure 1.** (a) Turbidity as a function of heating time for Indulin AT solutions with different concentrations of NaCl at pH 10.5 and 75 °C: (●) 0.6, (○) 0.8, and (▼) 1.0 M. At 0.8 M NaCl, Indulin AT starts to form clusters and to precipitate after a while. At 1.0 M NaCl the aggregation starts immediately as the sample is heated. (b) Turbidity versus time for Curan 100 solutions with different concentrations of NaCl at pH 10.5 and 75 °C: (●) 1.0, (○) 1.2, (▼) 1.3, and (▽) 1.4 M.



**Figure 2.** Turbidity versus NaCl concentration for Curan 100 and Indulin AT solutions after 10 min at 75 °C and pH 10.5: (●) Curan 100 and (○) Indulin AT. Indulin AT starts to form clusters and precipitate at much lower NaCl concentrations than Curan 100.

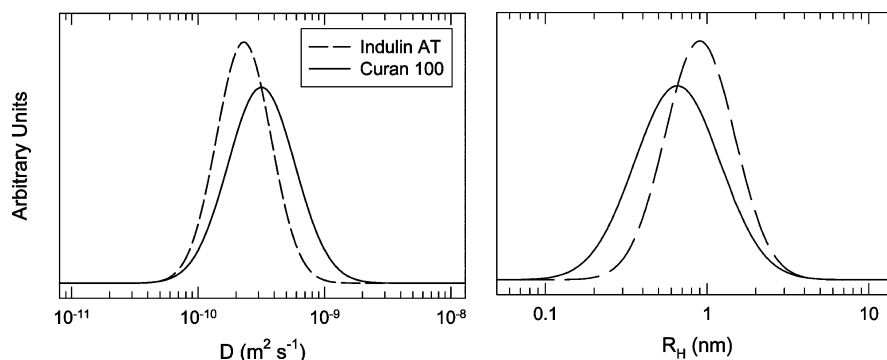
a NaCl concentration of 1.4 M before it starts to precipitate. The results follow the same trends as shown in Figure 1a,b.

Generally, at otherwise equivalent solution conditions, the solubility and stability of polymers and polyelectrolytes decrease by increasing molar mass. One explanation for this is that the loss of chain entropy is much lower when going from soluble to solid phase for high molar mass polymers than for polymers of lower molar mass. In the case of polyelectrolytes the electrostatic counterion binding is stronger for high molar mass polyelectrolytes than for low molar mass polyelectrolytes, and the entropy gained from counterion release is thus reduced in the former case.

To better understand the solution behavior of a charged macromolecule it is important to determine the size distribution. A fast and nondestructive method to examine differences in size between lignin samples is  $^1\text{H}$  PFG NMR self-diffusion measurements.<sup>12–14</sup> Figure 3 shows the mass-weighted distribu-

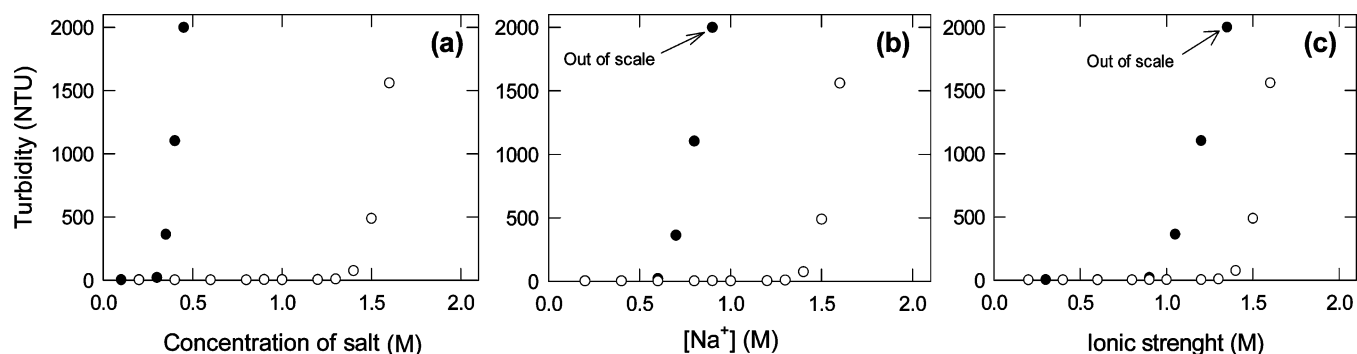
tion of self-diffusion coefficients and the corresponding distribution of hydrodynamic radii for the Curan 100 and the Indulin AT samples, obtained from the evaluation of  $^1\text{H}$  PFG NMR data. From the outcome it is clear that Curan 100 consists of smaller KL macromolecules than the Indulin AT sample. By considering the results in Figure 3, the outcome of the salt study presented in Figures 1–2 is more easily understood; KL macromolecules of smaller size (lower molar mass) require higher salt concentrations before they precipitate than high molar mass KL macromolecules do. This has also been shown in earlier studies.<sup>13</sup> Another important thing, valid specifically for KL, is that the charge-per-monomer ratio increases as the molecular mass decreases.<sup>12</sup> Indeed, this is a driving force for increased solubility for instance during kraft cooking. To be able to improve the yield of KL during precipitation, this also further strengthens the importance of better insights how to handle the most difficult fraction (low molecular KL) efficiently.

Figure 4a shows the turbidity for Curan 100 solutions plotted versus concentration of salt after 10 min of heating at pH 10.5. There is a large difference between the effects of NaCl and  $\text{Na}_2\text{SO}_4$ ; a lot more NaCl than  $\text{Na}_2\text{SO}_4$  is needed to precipitate the KL. Figure 4b shows the turbidity plotted versus the sodium ion concentration. Still, a large difference between the effects in the two samples is seen. In Figure 4c the turbidity is plotted versus the ionic strength of the used electrolytes at the same conditions as before. From the results shown in Figures 4a–c it can be concluded that neither the difference in the concentration of sodium ions nor the difference in valency between the anions can fully explain the relatively large difference in KL aggregation onset between the two salts. This indicates that there are specific interactions between KL and sulfate ions that govern the precipitation.



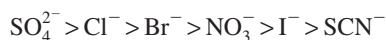
**Figure 3.** Lognormal distributions of self-diffusion coefficients, (to the left), and hydrodynamic radii, (to the right), for Indulin AT and Curan 100 showing a comparably lower molecular mass of the latter KL derivative.





**Figure 4.** Turbidity of Curan 100 solutions after 10 min in 75 °C at pH 10.5 versus (a) salt concentration, (b) sodium concentration, and (c) ionic strength. Notations: (●) Na<sub>2</sub>SO<sub>4</sub> and (○) NaCl.

The results further strengthen earlier studies that have shown that KL precipitation follows the inversed dependence of the Hofmeister series for anions,<sup>7</sup> that is, among the studied anions lignin precipitation is most readily induced by sulfate ions and decreases as follows:

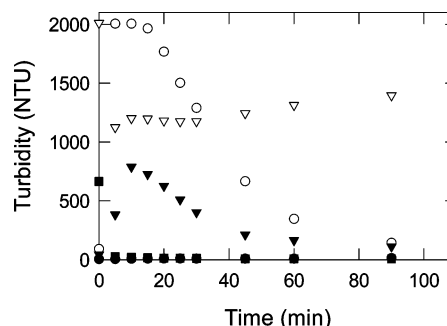


Since the aggregation kinetics is different, this further indicates that the structure of the lignin aggregate particles obtained from precipitation by different salts will be different and thereby also the filtration resistance. This has also been seen in other studies.<sup>15</sup>

**Effect of Surfactants.** The effect of surfactants on KL precipitation was performed mainly with Curan 100 as a model for KL. A constant concentration of NaCl, 1.0 M, was used in every sample. At that salt concentration the system was found relatively close to instability, whereby the different effects of the surfactants could be detected easily.

Among the investigated nonionic surfactants, the ones with polyoxyethylene head groups were found to give rise to relatively high turbidity values during the heating; for example, Berol 02, Berol 296, and Brij 56. At sufficiently high concentrations of these surfactants the samples start to aggregate already before heating. Cationic surfactants induced a relatively rapid KL aggregation, and high turbidity values were obtained during the experiment. The differences in aggregation of Curan 100 in the presence of different nonionic, cationic, and anionic surfactants are shown in Figure 5. Here, the sugar surfactant (AG 6210) and two polyoxyethylene surfactants (Berol 02 and Brij 56) are representing the nonionic surfactants, DoTAC and DoBS are representing the cationic and anionic surfactants, respectively.

In Figure 5 it is shown that the ethoxylated surfactants give rise to relatively high turbidity values initially and a relatively rapid settling, indicating formation of dense particle clusters. On the other hand, AG 6210 does not induce any changes at all and the tested anionic surfactant (DoBS) does not affect the sample much. However, the cationic surfactant (DoTAC) induces comparably high turbidity values. Due to DoTAC's positive charge, complex formation by electrostatic interactions with the anionic lignin structures (and thereby an increase in entropy of the counterions) is possible and thus the probable explanation of the increased turbidity. It can further be noticed that the cationic surfactant-lignin clusters do not settle during the experimental time, indicating that the clusters are of lower density than the precipitates obtained in samples containing nonionic surfactants. The relatively low rate of precipitate sedimentation in the mixtures of cationic surfactants and KL might also point to that the particle clusters are stabilized by the cationic surfactant.



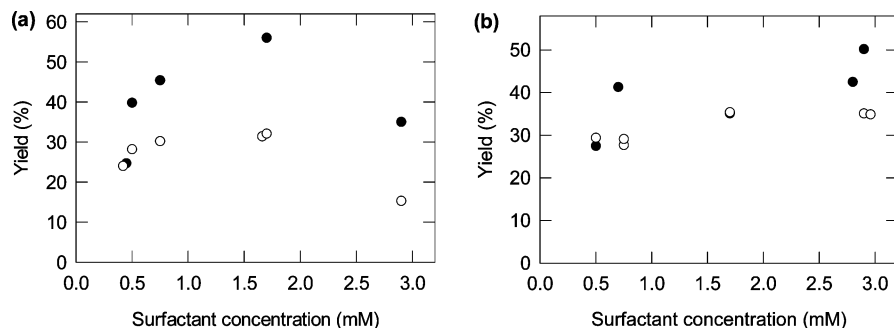
**Figure 5.** Turbidity as a function of heating time for Curan 100, 1.0 M NaCl and different surfactants at 2.0 g L<sup>-1</sup> at pH 10.5 and 75 °C: (●) AG 6210 (nonionic), (○) Berol 02 (nonionic), (▽) dodecyltrimethylammonium chloride (DoTAC, cationic), (■) dodecylbenzene sulfonic acid (DoBS, anionic), and (▼) Brij 56 (nonionic). With Berol 02, the KL show fast self-aggregation and precipitation, and a relatively high yield, about 50%, is obtained. AG 6210 shows no precipitated lignin at all after 90 min. DoBS, the anionic surfactant gives no effect either. The turbidity values for Brij 56 and Berol 02 decreases by time due to settling of precipitated lignin. DoTAC makes the lignin molecules to aggregate fast, but the aggregates do not settle.

**Table 2. KL Precipitate Yields after Addition of Different Surfactants at 1.0 M NaCl, i.e., below the Critical Coagulation Concentration (CCC) for Curan 100, and pH 10.5.<sup>a</sup>**

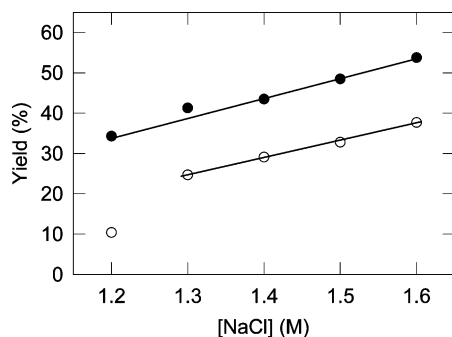
| surfactant | concentration (g L <sup>-1</sup> ) | yield (%) |
|------------|------------------------------------|-----------|
| AG 6210    | 0.5                                | <5        |
|            | 2.0                                | <5        |
| Brij 35    | 0.5                                | 24        |
|            | 2.0                                | 31        |
| Brij 56    | 0.5                                | 28        |
|            | 2.0                                | 35        |
| Brij 58P   | 0.5                                | 25        |
|            | 2.0                                | 56        |
| Brij 96V   | 0.5                                | 41        |
|            | 2.0                                | 43        |
| Berol 02   | 0.5                                | 19        |
|            | 2.0                                | 50        |
| Berol 296  | 0.5                                | 19        |
|            | 2.0                                | 48        |
| DOAB       | 0.5                                | 10        |
|            | 2.0                                | 26        |
| DoBS       | 0.5                                | n.d.      |
|            | 2.0                                | n.d.      |
| DoPyB      | 0.5                                | 7         |
|            | 2.0                                | 71        |
| DoTAC      | 0.5                                | 16        |
|            | 2.0                                | 72        |

<sup>a</sup> The Concentration of the KL Stock Solution was 10 g L<sup>-1</sup>. Notations: n.d. (not detected).

From the obtained experimental results it is indicated that if the initial aggregation (nucleation) creates large KL clusters,



**Figure 6.** (a) Precipitate yield versus surfactant concentration for Curan 100. (●) Brij 58 and (○) Brij 35. Conditions: 1.0 M NaCl; KL concentration, 10 g L<sup>-1</sup>; pH, 10.5; temp, 75 °C; and heating time, 90 min. Both the surfactants induce maximum KL precipitation at an approximate surfactant concentration of 1.7 mM. Note, the highest concentration of surfactant does not give rise to the highest yield. (b) (●) Brij 96 and (○) Brij 56. Conditions: 1.0 M NaCl, KL concentration, 10 g L<sup>-1</sup>; pH, 10.5; temp, 75 °C; and heating time, 90 min. In this case, the precipitation yields increase as the concentration of surfactants increase. Note that the concentrations of added surfactants are all well above the critical micelle concentration (cmc) for the surfactants.



**Figure 7.** Yield as a function of sodium chloride concentration for two different Curan 100 systems: (●) Curan 100 with Berol 02 (1.0 g L<sup>-1</sup>) and (○) Curan 100 without surfactant. The figure shows that the addition of this surfactant to the system gives an additive effect on the yield of precipitation. The straight lines in the figure are only for guidance to the eye.

the following self-aggregation will most probably induce precipitates of lower densities that settle relatively slow.

**Yield of Kraft Lignin Precipitation.** Table 2 shows the different precipitate yields obtained at two concentrations of the different surfactants. The results are based on single measurements on samples mixed from the same KL stock solution and thereby comparable from a quantitative viewpoint within the sample series. It is interesting to note that the effect of the cationic surfactant on the yield is most tightly connected to the added amount. One explanation could be that the interaction induces an increase in entropy in the system by the release of counterions from both the surfactant and the KL, followed by an increase in hydrophobicity that promotes the precipitation.

Since KL is a negatively charged macromolecule at the chosen experimental conditions in this study, attractive electrostatic interactions with the cationic surfactants give rise to an increased aggregation due to the increased hydrophobicity of the KL, and thereby relatively high yields. Among the

nonionic surfactants tested, large differences in the yield of precipitation can be noticed. Polyoxyethylene surfactants containing a phenyl group; Berol 02 and Berol 296, induce relatively high yields, whereas AG 6210, which is comprised of a glycoside ring attached to the hydrocarbon chain, induces very low degrees of precipitation (yields below 5%).

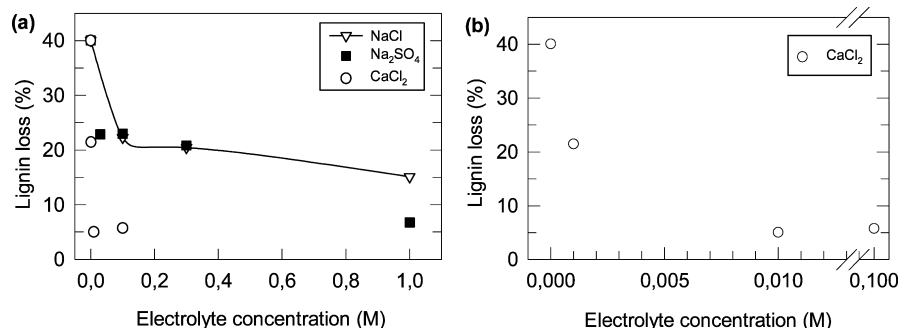
The yield differences between the samples containing different Brij surfactants are relatively large, as is seen in Figure 6a,b. The surfactants in the Brij series consist of hydrocarbon chains of different chain length and head groups with different number of oxyethylene groups. Brij 96 and Brij 56 have 10 ethoxylated groups and 18 and 14 carbon atoms, respectively, in the hydrocarbon chains. Brij 58 and Brij 35 have 14 and 12 carbon atoms, respectively and about 20 oxyethylene groups. As seen in Table 2, there is no clear correspondence between either the number of oxyethylene groups in the surfactants or the number of carbons in the chains and the yield of precipitation. The HLB-numbers (hydrophile–lipophile balance) as well as the molar masses for Brij 96 and 56 are lower than for Brij 58 and Brij 35. Concerning the Brij surfactants, cloud-point induced nucleation cannot be expected, since the cloud points for these surfactants are clearly above 75 °C. One explanation could be that specific polar interactions between the oxyethylene head groups and KL, similar to the lyotropic effects induced by, for example, sulfate, cause an increase in the hydrophobicity of the surfactant–lignin complex and, thus, an increased degree of precipitation. Hofmeister or lyotropic effects are not only caused by ionic substances. Monosaccharides and urea are examples of organic molecules known to induce such effects.<sup>9</sup>

Figure 7 shows the precipitate yield of Curan 100 at different concentrations of NaCl with and without the addition of Berol 02 at a concentration of 1.0 g L<sup>-1</sup>. The addition of the surfactant gives an increase in the precipitate yield of about 45% at these conditions.

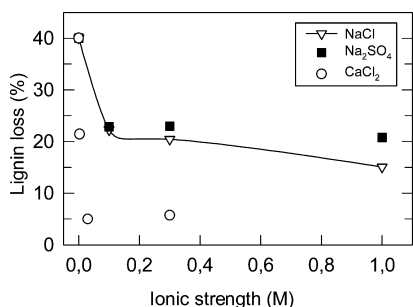
In Table 3, turbidity data of the precipitation of Curan 100 solutions containing three different nonionic surfactants at 1.0 g

**Table 3.** Turbidity Values of Three Different Surfactants in a Solution of Curan 100 with Different Concentrations of NaCl at 10 and 90 min; Initial pH = 10.5

| surfactant (1.0 g L <sup>-1</sup> ) | time (min) | turbidity (NTU) |            |            |            |            |
|-------------------------------------|------------|-----------------|------------|------------|------------|------------|
|                                     |            | 1.2 M NaCl      | 1.3 M NaCl | 1.4 M NaCl | 1.5 M NaCl | 1.6 M NaCl |
| Berol 02                            | 10         | 1656            | 1791       | 1350       | >2000      | >2000      |
|                                     | 90         | 468             | 421        | 479        | 474        | 575        |
| Berol 296                           | 10         | 1068            | 1388       | 1450       | >2000      | 1920       |
|                                     | 90         | 647             | 1203       | 1369       | >2000      | 1912       |
| Brij 56                             | 10         | 1149            | 1098       | 1752       | 1122       | 1339       |
|                                     | 90         | 506             | 600        | 853        | 716        | 742        |



**Figure 8.** Lignin loss versus concentration of different electrolytes during washing of KL precipitated from a Curan 100 solution at 70 °C (pH 10.5).



**Figure 9.** Lignin loss plotted against the ionic strength of the different electrolytes.

$L^{-1}$  and at five different concentrations of NaCl, are shown. From the turbidity values it can be noticed that the samples containing Berol 296 show relatively slow sedimentation rates. Even after 90 min, the turbidity is mostly higher than 1000 NTU in the samples containing Berol 296 regardless of the NaCl concentration. This points to that the aggregates are relatively large and that the cluster density is probably not too far from the density of the solution. Samples containing Berol 02 and Brij 56 show much lower end-turbidities than Berol 296, which indicates that the precipitate structures formed in the former samples are more compact than in samples containing Berol 296.

**Washing of Precipitates.** In Figures 8a,b, the lignin losses during washing of KL precipitates with different electrolytes at different concentrations are shown. The mass of a typical KL precipitate prior washing was about 2 g. The precipitates were washed three times with 167 mL of the fresh washing solution under rigorous mixing.

After each centrifugation, the supernatants were gently removed and collected and after three washing steps, the spent washing liquors (500 mL) were analyzed by UV-spectrophotometry to determine the amount of dissolved lignin. As can be seen in Figure 8a,b, the effect of calcium chloride additions to minimize lignin loss in precipitate washing is superior compared with the effects of the sodium-based electrolytes investigated. At a concentration of 1.0 mM, the lignin loss is reduced by roughly 50% and at 10 mM the lignin loss is about one tenth of the loss obtained in samples washed with Milli-Q water.

Figure 9 shows the outcome of the washing experiments from the point of ionic strength dependency. From Figure 9 it can be seen that the interaction between sodium ions and KL is quite well described in terms of screening, while the interaction between calcium and KL indicates strong ion binding or complex formation between the negative charges (free phenolic and carboxyl groups) of the KL macromolecules and the divalent calcium ions. It should however be pointed out that due to the method used, the washing of the precipitates had to be performed

with electrolyte solutions at room temperature, thereby, lyotropic effects of the different anions were suppressed and could not be detected.<sup>9</sup> Washing of the precipitates was also performed with liquors containing one of the surfactants used in the precipitation study (Berol 296). However, at room temperature the surfactant addition in the washing liquor did not lower the lignin losses further.

## Conclusions

This investigation shows that use of certain surfactants and salts containing specific inorganic anions dramatically increase the yield of precipitated KL. Sulfate ions show a more pronounced interaction with KL than chloride ions do, leading to precipitation at much lower concentrations. Among the surfactants, the effects of cationic surfactants are the most obvious, but nonionic surfactants give rise to relatively high increase in yields of precipitation already at relatively low concentrations. Moreover, the results indicate that the structure and the density of the precipitates formed are very different depending on the type of the surfactant. This is important to be aware of during separation, washing, and dewatering of the precipitates. The reason for the differences in precipitate structure is most probably originating from the initial mode of aggregation (“nucleation”). To further sort this out, a method for precise determination of the precipitate structure is needed. In the case of washing of KL precipitates, calcium chloride added to the washing liquor shows a pronounced reduction in the yield loss already at very low concentrations (millimolar region) compared with Milli-Q water or washing liquors containing sodium salts.

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