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Aggregation of Lignin Derivatives under Alkaline Conditions. Kinetics and Aggregate Structure

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The kinetics of kraft lignin (KL) aggregation at alkaline conditions was studied by quasi-elastic light scattering (QELS) and turbidity measurements. Stability ratios (W) for KL were obtained at 70 °C and various concentrations of sodium chloride. By analyzing the early-time evolution data of aggregate growth obtained from QELS, fractal dimensions of flocs formed in both reaction-limited cluster–cluster aggregation regimes and diffusion-limited cluster–cluster aggregation regimes were determined. Correlations between the fractal dimension and the W -ratio were found in accordance to recent studies of a system containing monodisperse polystyrene colloids. By cryogenic transmission electron microscopy, the fractality of KL aggregate structures in the system was also shown. It was seen from stability studies of KL solutions that the effects of specific co- and counterions follow the Hofmeister series. From the outcome of the investigation, different modes of aggregation occurring in a KL system are proposed. Starting from the macromolecular state of KL and evolving through larger aggregates, the KL clusters finally exhibit a supramolecular structure similar to what earlier has been proposed for native softwood lignin.

Introduction

Process control is often a nontrivial everyday issue in the manufacturing of many products. Knowledge of how to obtain and maintain stability in the various colloidal systems appearing is a necessity both for cost-effective production and in order to manufacture high-class products. In chemical pulping, the main goal is to remove as much as possible of the lignin from wood without destroying the polysaccharides. Lignin is a high molecular weight solid compound in woody plants, biosynthetically formed through reactions mainly between subunits of *p*-phenylpropanoic origin.¹ In today's most important chemical pulping process, the *kraft process*, aryl–ether bonds between the subunits in the lignin structure are cleaved by nucleophilic attack of hydrogen sulfide ions at high alkalinities and elevated temperatures. After the lignin in the fiber wall is depolymerized, which involves formation of kraft lignin (KL) fragments of various compositions, the KL is solubilized by dissociation of phenolic groups, due to the alkaline conditions in the digester. The KL fragments formed are thus widely polydisperse, both chemically and physically. For example, generally high molecular weight KL fragments might be considered having their pK_a 's at much higher levels than low molecular species.²

Apart from the chemical reactions needed for the depolymerizing of lignin structures, kraft pulping involves several steps of physicochemical origin, such as ionization, solubilization, and mass transport of cooking chemicals, polymers, and colloids. However, in comparison to the

efforts applied on elucidating lignin structures and reactivity within the traditional wood chemistry, the research activity focused on the above-mentioned phenomena has been relatively low. The polydispersity of KL will of course also introduce differences in the solubility characteristics within the macromolecular distribution of fragments. Earlier, it has been shown that in the presence of high concentrations of monovalent metal ion salts at pH neutral conditions, KL starts to coagulate and finally precipitate.³ Moreover, by elevating the temperature in alkaline KL solutions the dissociation of phenolic groups decreases, sometimes to levels below the threshold of solvency.⁴ Some studies dealing with the colloidal behavior of lignin derivatives have earlier been presented in the literature.^{3–10} From the work of Lindström, it is found that colloidal KL, in conformity with other colloids, exhibits a strongly marked critical coagulation concentration of added electrolytes (CCC).⁵ More recent, Norgren et al. showed that the experimentally observed phase behavior of colloidal KL can be described reasonably well by a theoretical approach derived from the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.⁴

In general, aggregation of colloidal particles into larger clusters has been a subject of serious scientific studies for more than a century. For aggregation due to Brownian motion, two well-defined limiting regimes of kinetics have been identified. These are rapid diffusion-limited cluster–

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cluster aggregation (DLCA) and slow reaction-limited cluster-cluster aggregation (RLCA).^{11–18} DLCA is the result of negligible repulsive forces between the colloidal particles, following the von Smoluchowski equations, thus causing particles to stick upon contact and to form loosely jointed and highly disordered structures. In case of RLCA, the sticking probability is much lower due to a substantial repulsive force between the particles, so that several collisions are possible before the particles finally aggregate. The creation of somewhat denser aggregates is characteristic in the RLCA regime. It has further been shown that the described processes are universal in the sense that they are independent of the detailed nature of the colloid, if the essential physical interactions are the same.¹¹ The mentioned two classes of aggregation processes and their crossover behavior are suggested to be sufficient to describe the complete range of kinetic aggregation.¹³ Since Mandelbrot¹⁹ introduced the term *fractal* to describe the noninteger dimensionality, exhibited by various common and very complex structures in nature, studies involving computer simulations have played a major role for the understanding of such phenomena.^{13,15–17}

Aggregation kinetics is often quantified in terms of stability ratios, W , defined as the ratio of the rate constant for DLCA to the experimentally determined rate constant for formation of doublets.^{20,21} As the ionic strength in the system increases, the stability ratio approaches unity, which is where the CCC of an electrolyte is most strictly defined. A theoretical W can be calculated by integration of an assumed total interaction potential, which might be derived from the DLVO theory.^{20,21}

In colloid science, the analysis of mass fractal dimensions of aggregates has shown to be a good discriminator in distinguishing between different aggregation processes. For DLCA, the mass fractal dimension often is found to be around $d_f \approx 1.8$, while in the case of RLCA aggregate d_f is usually situated around 2.1.¹⁴ Much concern has been devoted to RLCA, due to the existence of a stability threshold in this regime. A great source of understanding has been adopted from the relative simplicity of the DLVO theory, which divides the forces of interaction into one attractive component, the van der Waals forces, and one repulsive part arising from the electrostatics.^{20,21} However, additional stabilizing effects may also be attributed, and a good example of this is the concept of steric stabilization, thoroughly described by Napper.²² Electrosteric stabilization, which is a combination of both electrostatic and

configurational entropic repulsive forces between colloidal particles, gives sometimes an explanation of why some colloidal dispersions still are stable at high ionic strengths and elevated temperatures. Usually either surfactants or polymers have to be added to a colloidal system to obtain these effects. Concerning KL, only one investigation, to the knowledge of the authors, demonstrating this kind of stabilization mechanism has earlier been presented.²³ However, to the authors' knowledge, no results concerning the kinetics of KL self-aggregation have earlier been reported. Information on the criteria of system stability is very important in order to understand the physicochemical fundamentals of KL self-aggregation. Industrially, this might also be a prerequisite for successful process control. Therefore, the objectives of the present investigation have been to investigate macromolecular and colloidal properties of KL by means of determining the self-aggregation kinetics at some specific solution conditions and the information related to this.

Experimental Section

Materials. A commercial softwood KL (KLI, Indulin AT, lot 123H0189, $M_n = 1060 \text{ g mol}^{-1}$, $M_w/M_n = 5.2$ determined by SEC²) was supplied by Aldrich. All metal salts used were of analytical grade and supplied by Riedel-deHaën. Coniferyl alcohol, HPLC-grade, was delivered by Aldrich. Deionized water was used throughout the investigation.

In the ^1H pulsed field gradient (PFG) NMR studies, 0.1 M NaOH was used as the solvent for the KL samples. Filtron Omegacell stirred cells with polyethersulfone membranes that were used in the ultrafiltration had nominal molecular weight cutoffs of 1 and 100 kDa. Sample capacity was 150 mL with a filter area of 23.2 cm² and a hold-up volume of <0.7 mL. The nitrogen pressure was set to 275 kPa, and the stirrer speed was 250 rpm. The sample was dissolved and ultrafiltered in 0.1 M NaOH.

Methods. Preparation of Sample Solutions. The various KL solutions were prepared by a total addition of 0.012% NaOH in water, and after a few minutes, small portions of deionized water up to about 50% of the desired total volume were added. The KL was allowed to dissolve overnight under magnetic stirring. Additions of metal salts were made, and the pH in the samples was adjusted to an appropriate value by 2 M HCl or 2 M NaOH. During the experiments, the samples were heated in a temperature-controlled water or oil bath or in an oven.

Turbidity Measurements. The turbidity was determined using a Hach RATIO/XR 43900 turbidimeter, equipped with a tungsten lamp and operating at all the wavelengths of visible light. All measurements were performed directly on the warm sample cuvettes. The difference in turbidity between a newly heated, still hot sample and the equivalent sample, first heated and chilled and then stored at room temperature for several weeks, was found to be below 10%.

Quasi-Elastic Light Scattering (QELS). QELS was performed with a Brookhaven model BI-200SM goniometer, a Brookhaven model BI-9000AT correlator, and a Lexel 300 mW Ar laser. Experiments were performed at 25 and 70 °C, and the response signal from the detector was analyzed once per minute or every second minute, depending on the rate of aggregation. In the analysis, the average from 15 s of scattering time was used and the autocorrelation functions were analyzed by the method of cumulants.²⁴ The apparent hydrodynamic diameters were obtained from the measured diffusion coefficients using the Stokes–Einstein relationship. In a polydisperse system, results from QELS measurements give more or less the diameters of the largest aggregates and not a weight average or size average.

^1H Pulsed Field Gradient NMR. Self-diffusion measurements were performed at 20 °C on a Bruker DPX 250 MHz spectrometer, equipped with a Bruker self-diffusion probe capable of providing magnetic field strengths up to 3.0 T m⁻¹. The experimental settings were $\Delta = 70 \text{ ms}$, $\delta = 1.3 \text{ ms}$, and $g \in [0.4, 1.55] \text{ T m}^{-1}$,

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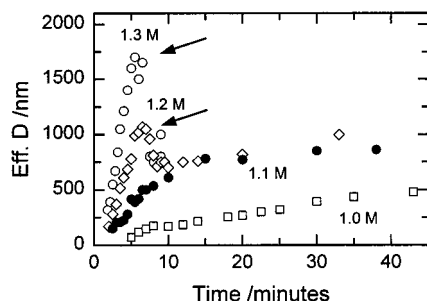


Figure 1. Hydrodynamic diameters of KL aggregates as a function of time and sodium chloride concentration at pOH 3.5 and 70 °C. The aggregation rate increases with increasing salt concentration. At and above 1.2 M NaCl, obvious settling at apparent aggregate diameters above 1000 nm can be detected (arrows).

and a stimulated-echo sequence²⁵ was applied with a 3.0 s delay time between subsequent scans (32 scans). The echo intensities (24 points/experiment) obtained from the measurements were analyzed by Matlab, and the echo decays were found to satisfy log-normal distribution functions of self-diffusion coefficients.²⁶

Cryogenic Transmission Electron Microscopy (cryo-TEM). A Philips CM120 BioTWIN Cryo equipped with a Gatan Energy Filter GIF 100 was used in the study. The microscope was operating at 120 kV in low-dose mode, and the photographs were taken utilizing the zero loss peak at a slit width of 8 eV. The cryo-holder was an Oxford CT 3500, and the samples were plunged into liquid ethane.^{27,28} The working temperature of the TEM was kept below −175 °C.

Results and Discussion

The stability in colloidal systems is dependent on the delicate balance between repulsive and attractive forces.²¹ In a recent study, the phase behavior of KL (Indulin AT) was investigated and precipitation curves at various alkalinities were experimentally and theoretically determined.⁴ An indirect measure of the net interparticle interactions, as quantified by the change in hydrodynamic particle size, can also be determined from investigations of the aggregation kinetics. From the kinetics of aggregation, stability ratios (*W*-ratios) reflecting the stability threshold at various ionic strengths can be derived.²⁰ Moreover, information on the aggregate structure might be obtained as well as indications of the modes of aggregation in the system.^{11–18}

Aggregation Kinetics. Figure 1 shows the kinetics of KL aggregate formation and growth, as followed by QELS. The measurements were performed at 70 °C, alkaline conditions, and different sodium chloride concentrations, as indicated in the figure legend. At higher ionic strengths, very large aggregates are formed. Consequently, some samples are found to be settling during the time of experiment. In the interval [NaCl] ∈ [1.3, 1.5] M, the aggregation curves are found to be overlapping. At a sodium chloride concentration of 1.5 M, samples are starting to phase-separate already at room temperature. Turbidity measurements at lower salt concentrations reveal that the onset of KL coagulation is detected at a sodium chloride concentration of approximately 0.35 M at 75 °C and pH = 10.2. This is found to be independent of the KL concentration in the samples studied (Figure 2). From the analysis of early-time kinetics in Figure 1,

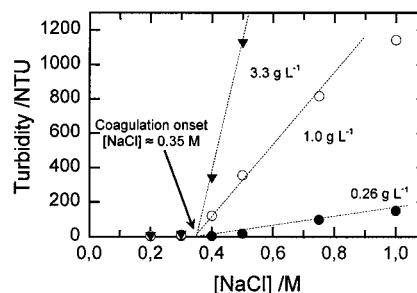


Figure 2. End-turbidity after 44 h at 75 °C as a function of time and sodium chloride concentration at pOH = 3.8. The coagulation onsets show no significant dependency on the KL concentration in the interval 0.26–3.3 g L^{−1}.

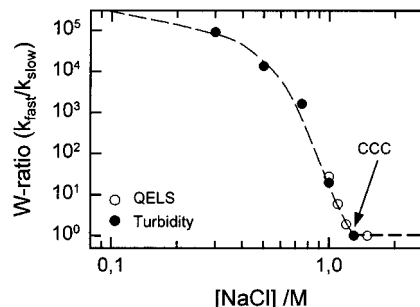


Figure 3. Stability ratio of unfractionated KL as a function of NaCl concentration at pOH 3.5 and 70 °C. The CCC is 1.3 M.

aggregation rate constants at various sodium chloride concentrations can be derived. By assuming diffusion-limited aggregation at the highest ionic strength ([NaCl] = 1.3 M), *W*-ratios were calculated according to method of Reerink and Overbeek.²⁰ As a complement to the QELS measurements, turbidity was used to monitor the coagulation rate at lower salt concentrations. In Figure 3, the determined *W*-ratios for the KL system at given solution conditions are shown. As shown in Figure 3, the correlation between the two different light-scattering methods is very good. Interestingly enough, in the sodium chloride concentration interval of 0.2–0.7 M, the stability curve shows a gradual change in that the curve levels out and a much lower slope than observed at higher ionic strengths is obtained. As discussed earlier, the onset of coagulation determined by turbidity can be found within this electrolyte concentration interval. In a previous investigation by Burns et al., a somewhat similar behavior was observed.²⁹ In that case, a system containing colloidal polystyrene latex particles in the presence of various concentrations of KNO₃ was studied. There, the onset of aggregation was found to be [KNO₃] = 0.28 M, while a potassium nitrate concentration of [KNO₃] = 0.70 M, defining the CCC, was detected.

Qualitatively, the slope of the stability curve might give some information on the height of the repulsive energy barrier according to the fundamentals of the DLVO theory.²⁰ As shown in eq 1, in an electrolyte solution containing monovalent counterions (*z* = 1), the

$$\frac{d \log W}{d \log C} = L \frac{R \Psi^2}{z^2} \quad L = 2.15 \times 10^7 \text{ m}^{-1} \text{ at } T = 298 \text{ K} \quad (1)$$

slope of the stability curve has a quadratic dependency of the Gouy–Chapman expression, $\Psi = (\exp(ze\psi_0/2kT) -$

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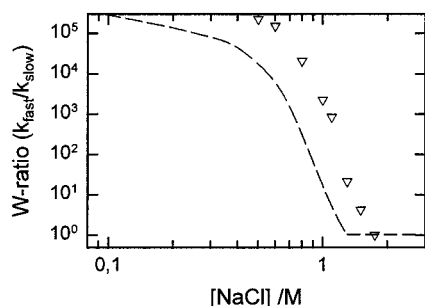


Figure 4. Stability ratio of ultrafiltrated KL ($1 < M < 100$ kDa) as a function of NaCl concentration at pOH 3.5 and 70 °C. The CCC of the fractionated sample is 1.75 M.

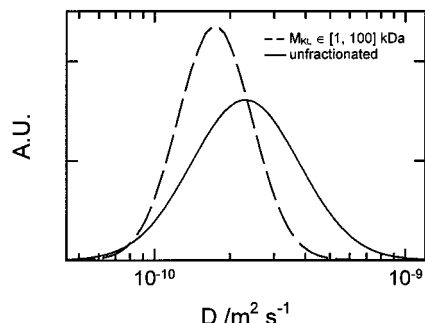


Figure 5. Log-normal distributions of self-diffusion coefficients in the two investigated samples. The ultrafiltrated KL sample shows both a narrower distribution curve and a lower mass-weighted median self-diffusion coefficient ($D_m = 1.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) than the unfractionated KL sample ($D_m = 2.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

$1)/(\exp(ze\psi_0/2kT) + 1)$.²¹ The radius of a colloidal particle is however proposed to be directly proportional to the slope. Considering a relatively constant surface potential (ψ_0), which might be obtainable if only minor changes in electrolyte concentration occur, eq 1 proposes a proportional increase in the particle radius as the slope of the stability curve becomes steeper. In the present investigation, the change in slope of the stability curve gives an indication of the different *modes of aggregation* in the system, which will be discussed in more detail later.

From the plots shown in Figures 1–3, it can be observed that very high concentrations of salt are needed to induce self-aggregation. Second, the KL system shows a dramatic response to relatively small differences in salt concentration. Even at very high ionic strengths (0.8–1.3 M) where the Debye screening length is very short ($\kappa^{-1} \approx 0.3 \text{ nm}$ at 70 °C) and the electrostatic repulsive barrier thus should be efficiently removed, an increase in salt concentration results in increasing rate of aggregation. A different but similar aspect on this kind of behavior is that both the chemical and physical heterogeneity of the KL macromolecules might interfere in terms of a diversified solvency.^{10,30} Normally, KL samples are widely polydisperse, and the stability curve presented in Figure 3 is obtained from such sample compositions. Figure 4 shows the outcome of W -ratio determinations on an ultrafiltrated KL sample ($1 < M < 100 \text{ kDa}$) where both the lowest and highest molecular weight residues have been removed. In Figure 5, the differences between the macromolecular composition of unfractionated and ultrafiltrated KL samples, as determined from log-normal distributions of self-diffusion coefficients obtained from evaluations of ^1H PFG NMR self-diffusion measurements, can be seen. As

would be expected, the ultrafiltrated sample shows a narrower distribution of self-diffusion coefficients than the unfractionated sample. The mass-weighted median self-diffusion coefficient is also lower for the ultrafiltrated sample. When the two different stability curves are compared, it is seen that the aggregation behavior of unfractionated and ultrafiltrated KL samples is similar in the sense that the curves are almost completely parallel. However, the fractionated KL sample consequently displays a higher stability than the unfractionated sample. One possible reason for this is that colloiddally unstable KL residues, important for the onset of aggregation, exist at “molecular weights” over 100 kDa in 0.1 M NaOH solutions. These species will then be removed by the first step of the ultrafiltration procedure and increase the stability of the solution. By ^1H PFG NMR self-diffusion measurements, it would not be possible to detect such colloidal material due to its very rapid T_2 relaxation. A completely different explanation could be that the presence of low molecular weight fragments destabilizes KL samples. This was tested by aborting the ultrafiltration procedure after the 100 kDa filter. However, no differences in the colloidal stability between these samples and the samples represented by Figure 4 could be detected. To further investigate the influence of low molecular weight phenols on system stability, coniferyl alcohol was added in different amounts to ultrafiltrated KL sample solutions at NaCl concentrations of 1.3 M and pOH 3.5. From the outcome of the test, no effect on the KL stability was detected up to a concentration range of 0.3 g L^{-1} coniferyl alcohol. Thus, this indicates the existence of a high molecular weight, dispersed KL material that is responsible for the decrease in the colloidal stability observed in the investigation of the unfractionated sample. This KL material is removed by the 100 kDa filter in the ultrafiltration procedure.

Differences in KL Colloidal Stability Connected to Various Monovalent Ions. Are KLS sterically stabilized? The explanation of (electro)steric stabilization, indicating nonelectrostatic contributions to the stability threshold, is described thoroughly by Napper.²² At varying ionic strengths, the combination of electrostatic and steric (electrosteric) stabilization is a nonunique phenomenon and is thus found even in systems more well-defined than the present KL system.²⁹ According to Napper,²² one way to examine the existence of steric interference in colloidal systems is to observe the aggregation behavior in the presence of various salts belonging to the so-called Hofmeister series.³¹ A generally accepted explanation of these ion specific effects is still not conceived. Depletion of ions from regions immediately adjacent to the polymers has been suggested as an important factor responsible for the salting-out phenomenon.²² By considering the interfacial tensions acting in a system, Ninham and Yaminsky³² have given a similar but deeper explanation of the phenomenon. They argued that the Hofmeister series will emerge naturally if both electrostatic and dispersion interactions are included in the complete (nonlinear) Gibbs adsorption equation.³²

In Figure 6a,b, the influence of some different cations and anions on KL system stability followed by turbidity measurements is shown. From Figure 6a, it can be seen that among the tested cations, the lowest stability is obtained in the presence of cesium ions. Within the series of tested metal ion chlorides, the mutual order in causing

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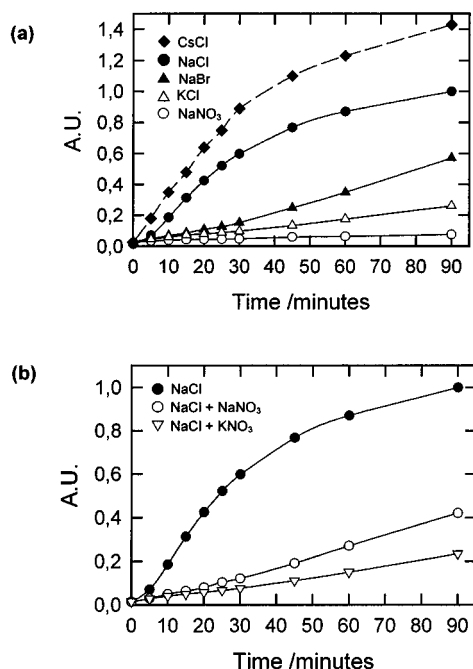


Figure 6. The effect of various monovalent metal ion salts on the stability of KL as monitored by turbidity measurements versus time. (a) The effect of various salts in the Hofmeister series is shown. In (b), the additive effect of anions and cations is demonstrated. Note: All turbidity values are normalized against the end-turbidity of the NaCl sample in each figure.

aggregation is found to be $\text{Cs}^+ > \text{Na}^+ > \text{K}^+$. Concerning the anions, the lowest KL stability is obtained for Cl^- , followed by Br^- and then NO_3^- . In comparison to the Hofmeister series, the outcome of the salt test presented in Figure 6a shows no correspondence for cations. Instead, the results follow the trend of atomic number for alkali metal ions in the periodic table, causing increased aggregation as the radii of the nonhydrated cations increase. On the other hand, for the investigated anions the outcome shows a strong correlation to the classical classification according to Hofmeister.³¹ By considering the work of Napper,²² these results indicate that the KL colloids in some way could be sterically stabilized against flocculation at higher ionic strengths. In a system of wood polymers, such electrostatic stabilization could be promoted by the lignin derivative itself or possibly by other polymeric substances, for instance, hemicellulose moieties adsorbing to colloidal lignin. Realistically, the former explanation seems the most probable in the case of the presently investigated KL systems. As discussed earlier, in a heterogenic KL system fragments of lower molecular weight participate in the aggregation process.^{10,30} If adsorption of KL macromolecules to colloidal KL occurs, the macromolecules could more or less oppose further aggregation sterically. Furthermore, the stability, which in this case would be due to the entropy and solubility of the chains, might then be unequally manipulated by different anions belonging to the Hofmeister series. However, clear evidence for this has been found neither in the present investigation nor in the literature.

As shown in Figure 6a, NO_3^- is the best and Cl^- is the worst among the tested anions in providing stability for the KL system. According to the Hofmeister series, organic anions usually are even worse than inorganic anions in destabilizing colloids. In this matter, the influence of very low molecular weight residues of hemicellulose, for example, sugar acids, on KL stability would be very interesting to investigate.

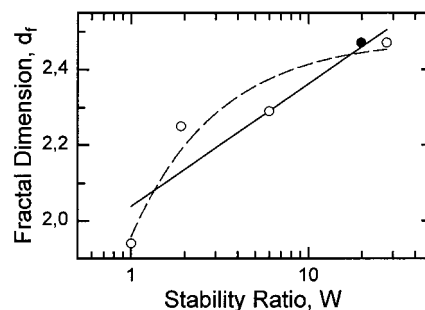


Figure 7. Fractal dimensions as a function of stability ratio. The straight line in the figure is derived from a linear regression of the data points and follows $D_f = 2.04 + 0.324 \log(W)$. The nonlinear curve represents an approximate correlation between d_f and W , considering limitations in spatial dimensions.

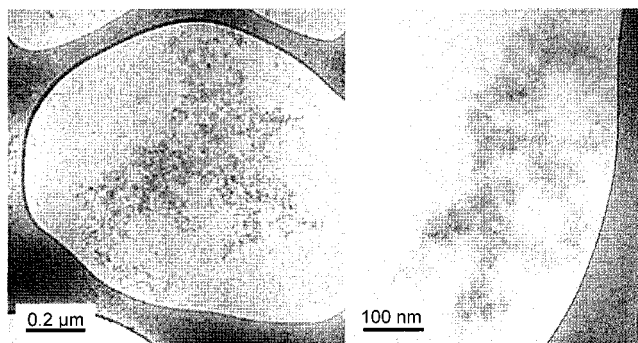


Figure 8. Cryo-TEM of unfractionated KL solutions showing fractal RLCA clusters. Aggregation conditions: $[\text{NaCl}] = 1.0 \text{ M}$, $\text{pOH} = 3.5$, $T = 70^\circ \text{C}$.

Figure 6b shows the aggregation behavior after additions of sodium chloride and alkali metal ion nitrates to samples containing a fixed standard sodium chloride concentration. As can be seen in Figure 6b, when sodium chloride is the only electrolyte, extensive aggregation by time occurs. In samples containing a mixture of both 0.375 M NaCl and 0.375 M NaNO₃ or 0.375 M KNO₃, the aggregation is much less pronounced. The outcome of the salt test clearly indicates that the effects of cations and anions in metal salts are to be considered as additive in the case of KL self-aggregation. This kind of behavior has earlier been proven as a general law concerning aggregation of colloids.²²

Aggregate Structure. As mentioned in the Introduction, the structure of a colloidal aggregate is very much dependent on the rate of aggregation. In RLCA regimes, the aggregates are found to be relatively compact and the fractal dimension (d_f) is thus the largest at high stability ratios. However, as the solution conditions get worse, the W -ratio decreases, and the system enters the DLCA regime, d_f decreases and the flocs formed get much "looser" in shape. Figure 7 shows a plot of d_f versus the stability ratio for the investigated KL system. The fractal dimensions are calculated by using the relation $R \propto t^{-d_f}$. The radius of an aggregate, R , is obtained from early-time QELS measurements.³³ As shown in Figure 7, the fractal dimensions for clusters in the investigated KL samples vary from about $d_f = 1.9$ up to about 2.45. The straight line in the figure is derived from linear regression of the data points, while the curve represents a more likely correlation dependency between d_f and W , if limitations in the spatial dimension are considered. Recently, Kim and Berg presented an investigation of charged polysty-

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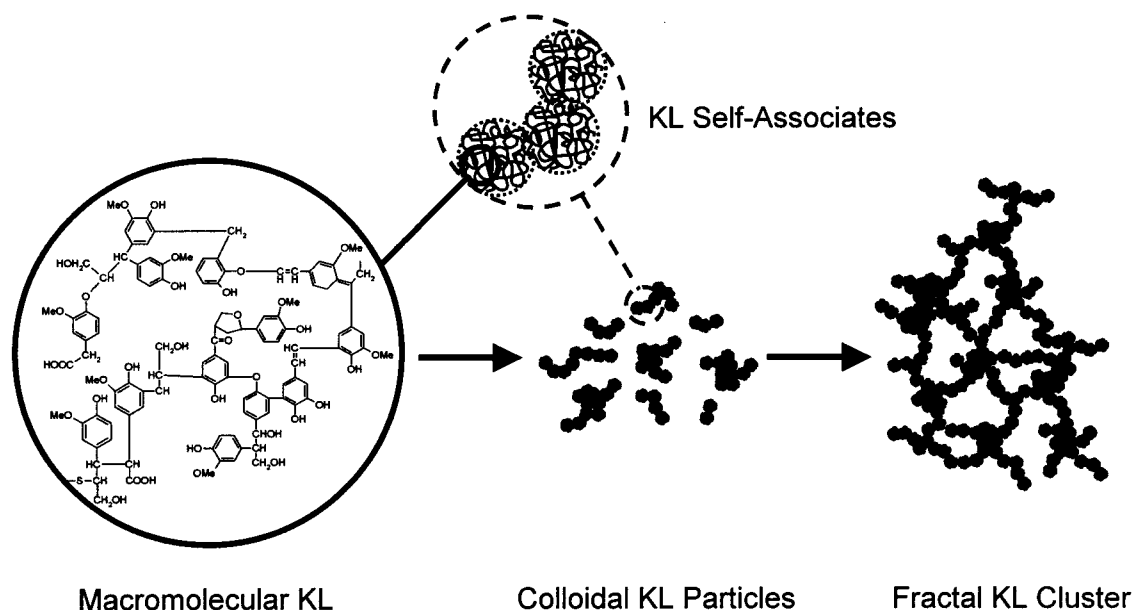


Figure 9. A schematic representation of the modes of aggregation in KL systems starting from macromolecular KL (ref 49) and finally reaching fractal KL clusters.

rene colloids undergoing aggregation.³⁴ In that study, a similar scaling between the fractal dimension and the stability ratio was found.

In Figure 7a,b, cryo-TEM photographs showing colloidal KL flocs as the results of extensive aggregation at $[\text{NaCl}] = 1.0 \text{ M}$, $\text{pOH} = 3.5$, and a temperature of 70°C can be viewed. The structure of the flocs clearly resembles the distinctive features of fractal patterns also seen in other aggregating colloidal systems.^{15,17,18,33} From the analysis of the cryo-TEM pictures, it is not possible to obtain precise information about the true size distribution of the clusters. It can however be stated that during these solution conditions, flocs in the order of about 100 nm up to about $1\text{--}2 \mu\text{m}$ might be formed. A very important aspect to consider, in context to kraft delignification, is that aggregates of such dimensions would be efficiently entrapped within the pulp fiber walls and the rate of delignification, described from a viewpoint of mass transportation, would thus be considerably reduced.

Interestingly enough, the configuration of the flocs visualized in Figure 8 resembles the description of the supramolecular structure of native lignin in the fiber wall proposed by others.^{36–44} For example, Gravitis suggested that the cell wall lignification proceeds from lignin macromolecule formation via chemical reactions following diffusion-limited aggregation (DLA), finally creating a network of polydisperse lignin aggregates exhibiting fractality.^{35,36} Furthermore, from the work of Houtman and Atalla,³⁷ Roussel and Lim,^{38,39} and Jurasek,^{40–42} this was adopted and visualized by computer modeling. By treating lignin removal during chemical pulping from the

perspectives of percolation theory,^{43,44} Leclerc and Olson were able to describe the delignification process and to extract fundamental physical data from their model.⁴⁵

Modes of Aggregation. The flocs with fractal structures shown in Figure 8 are the outcome of considerable KL aggregation. However, as a reminder, KL in the present system exists initially only as dissolved macromolecules, and during the aggregation process several minor steps must be involved before the “final” flocs are formed. From Haugs triangle,²¹ which roughly describes the different conformations adaptable for polymers in solution, it is found that at poor solution conditions the conformation of polymers is very dense. In the case of KL, especially high molecular weight fragments, the structure is cross-linked and the macromolecules are described as being spherical and adapting very compact conformations in various solvents.⁴⁶ Already in its macromolecular form, some of the high molecular weight KL may be considered as colloidlike. This is not due to its size but is most of all due to the low degrees of molecular freedom, which more correctly defines the colloidal state generally. In aggregation processes, the onset can be described in terms of nucleation.²¹ After forming nuclei, growth of colloidal seed-points proceeds more or less rapidly.⁴⁷ The possibilities of forming larger aggregates by flocculation of KL nuclei are thus conceivable. Concerning KL, high molecular weight macromolecules present in the system are the natural nuclei, that is, necessary surfaces for aggregation onset. Since adsorption always foregoes aggregation,⁴⁸ the latter description also provides an explanation for why low molecular weight KL fragments, otherwise soluble, would participate in this process at all. Furthermore, this approach also motivates the facilitation of heterogeneous coaggregation of low molecular weight KL fragments earlier observed in the presence of high molecular weight

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and/or colloidal KL particles.^{6,10,30} From the appearance of the stability curves presented in Figures 3 and 4, it can be seen that both in unfractionated, completely heterogeneous KL samples and in KL samples where the lowest molecular weight fragments have been removed by ultrafiltration, the start of aggregation is somewhat sluggish.

According to the present observations and by considering studies presented earlier, the modes of aggregation in the investigated KL system could be illustrated by the proposed scheme in Figure 9. When the solution conditions gradually get worse, macromolecular KL fragments⁴⁹ start to self-associate to form colloidal particles. These particles grow both in number and in size, and finally fractal KL cluster structures are formed. The compactness of the fractal structures varies due to the rate of aggregation. In the DLCA region, the clusters are relatively loose in their conformation and as the rate of aggregation decreases (*W*-ratio increases) denser clusters are formed.

Conclusions

Depending on the solution conditions, macromolecular KL may undergo phase transition and enter the colloidal state. If the solution conditions get worse, that is, if the hydroxide concentration decreases, or if the ionic strength or the temperature increases, formed colloidal KL particles will coagulate. The coagulation is however not only opposed by the electrostatics. This is clearly indicated by the diversified system sensitivity with respect to different kinds of anions. From a fundamental viewpoint, the aggregation behavior of the investigated KL system

appears similar to what sometimes is comprised as universality and, thus, observed in other completely different colloidal systems. The flocs formed show deviations in structural buildup. In this manner, different solution conditions induce divergences in sticking probability between KL particles. The detected differences in aggregate structure are best described in terms of fractal dimensions. From a process technology point of view, the outcome of the present investigation shows the importance of "tuning the chemistry" in the digester to increase solvency and to avoid the formation of irreversible KL flocs in the pulp fiber walls. The obtained results also contribute to the fundamental knowledge of KL solution behavior and provide some new insights for the explanations of some of the paradigmatic questions regarding the physicochemical properties of lignin in general. However, questions still arise, and further investigations dealing with the solution behavior of this very complex material are necessary, planned, and under way.

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