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Flocculation of Kraft Lignin Sols with Polyethylene Oxide

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Abstract

The flocculation of a specially prepared sol of kraft lignin by polyethylene oxide (PEO) was studied. The effects of polymer dosage, sol concentration, pH, and electrolyte addition (NaCl and $CaCl_2$) on the flocculation behavior were investigated. The efficiency of lignin removal increased with increasing electrolyte concentration, valency of the counterion, and decreasing pH of the sol. In all cases maximum flocculation occurred at an optimum polymer dosage (O.P.D.) which was found to be independent of pH and electrolyte concentration within the intervals studied. The O.P.D. (as percentage of the sol concentration) was found to be independent of the sol concentration. The mechanism of restabilization was studied by heating the stable dispersions to temperatures exceeding the θ-temperature of the PEO. The critical flocculation temperature was found to coincide with the θ-temperature of the PEO (enthalpic stabilization). The mechanism of flocculation is discussed and it is concluded that bridging occurs when the thickness of the electrostatic double layer is sufficiently reduced by addition of an electrolyte (sensitization flocculation) or by charge reduction on the particle surface (protonization).

INTRODUCTION

Kraft lignin constitutes the major color contaminant in kraft mill effluents.

The removal of lignin is not only of great importance from an ecological standpoint, but is also highly desirable in cleaning up process waters in a closed paper mill. The interference of lignin with retention aids, internal sizing, etc. is well known, and the impact of increased knowledge of how to remove lignin from water cannot be underestimated. Lignin also is a material which is used in several fields (*1*), and the process of reclaiming lignin from waste waters will probably be of increased importance in the future.

In this laboratory the colloidal behavior of a dialyzed kraft lignin fraction has been studied in detail (*2*). One of the results was a route to prepare stable kraft lignin sols in aqueous solutions. These sols have been carefully studied with respect to their coagulation behavior, and they are also suitable for flocculation studies.

It is known that it is possible to flocculate lignin derivatives from spent liquors in the pulp and paper industry (*3*) by addition of polyethylene oxide (PEO). However, the influence of variables such as pH and electrolyte concentration on flocculation behavior has not been thoroughly investigated.

The purpose of this paper is to report a study of the flocculation behavior of a kraft lignin sol with PEO. The results are interpreted in terms of current concepts of bridging flocculation and steric stabilization.

EXPERIMENTAL

A sample of a commercially available kraft lignin (Indulin ATR, 11037–2) manufactured by Westvaco Co., Charleston, South Carolina, was employed in this work.

Functional group content and structural units in similar products have been reported elsewhere (*4*). The high molecular weight fraction (sol fraction) of this sample was isolated by dialysis under alkaline conditions and subsequently ion-exchanged to its hydrogen form as previously described (*2*). This product contained no low molecular weight material (Fig. 1) as determined from GPC-measurements in DMF (*2*). The carboxyl group content was determined to be 1.3 ± 0.1 meq/g (*2*). The degree of dissociation (*2*) was varied by adding different amounts of NaOH to the lignin sol.

The lignin sol samples were prepared from a stock solution (≈ 10 g/l), which was stored in a refrigerator at 8 °C. These sols showed no visual turbidity.

Electron micrographs of the dried kraft lignin sol revealed that the unit particles (as visually determined) were irregularly shaped with sizes varying between 50 and 200 Å.

The polyethyleneoxide (PEO) used in this work was Polyox WSR 301 ($M_w \approx 4 \times 10^6$) manufactured by BDH Chemicals Ltd., Poole, United Kingdom.

All the inorganic electrolytes used in this work were of the highest

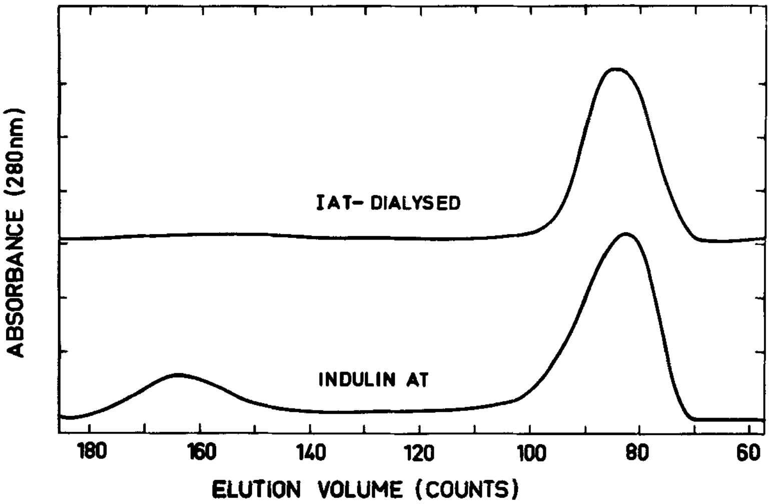

FIG. 1. Molecular weight distribution of the kraft lignin sample and the dialyzed fraction used in the experiment. GPC experiments were performed in dimethylformamide on a combined system with kraft lignin gels and Bioglas 2000. Details are described elsewhere (*2*).

commercially available grade. Distilled and deionized water exhibiting a conductivity less than $10^{-6}\,\Omega^{-1}\,\text{cm}^{-1}$ was used in all experiments. The following mixing procedure was found to yield reproducible results in the flocculation experiments.

Two test tubes were prepared. One contained 25 ml of the kraft lignin sol and the other 25 ml of the PEO solution. Both test tubes contained the desired concentration of simple electrolyte, except in the experiments where the critical flocculation temperature (C.F.T.) of the stable sols was determined. In these experiments 50 ml of the electrolyte solution was added after the lignin sol had been mixed with the flocculant.

The contents of the two test tubes were mixed slowly for 2 min, whereupon the mixture was vigorously shaken by hand for 60 sec. The samples were then allowed to stand for 1 hr. After subsequent centrifugation at ≈500 g for 15 min, a visually clear supernatant was obtained. The residual lignin concentration in the supernatant solution was determined by UV-absorption at 280 nm in a Beckman DB-G spectrophotometer.

The C.F.T. of the sterically stabilized dispersion was determined visually after 3 hr on a series of sols placed in a temperature profile. The transition point between long-term stability and flocculation was taken as the C.F.T. In this way the C.F.T. could be determined within ±2 °C. The adsorption of PEO onto the lignin dispersion was measured by a nephelometric method based on the turbidity produced when tannic acid is added to PEO (*5*). These measurements could not, however, be performed unless 0.5 *M* NaCl ($T < \theta$-temperature for PEO at this salt concentration) was added in order to aggregate the lignin sol completely, before tannic acid was added. Adsorption measurements must be regarded as indicative, as the polymer–solvent interaction is decreased by the addition of NaCl (i.e., the θ-temperature of PEO is lowered by NaCl).

RESULTS

Figure 2 illustrates the effect of pH or the degree of dissociation of the acidic groups of the lignin sol on the residual lignin concentration in solution after flocculation with PEO.

The O.P.D. is not affected by the degree of dissociation, but the efficiency of the removal of lignin diminishes with increasing pH. When all the acidic groups are dissociated (pH 6.2), the stability of the lignin sol is not affected by addition of PEO. However, these conditions only prevail under salt-free conditions.

The effect of electrolytes on the flocculation of a lignin sol by PEO at pH 6.2 ($\alpha = 1.0$) is illustrated in Fig. 3. The level of addition of PEO was 20 ppm (O.P.D.). As can be seen, lignin removal is strongly affected by the electrolyte concentration. The lignin removal also depends very

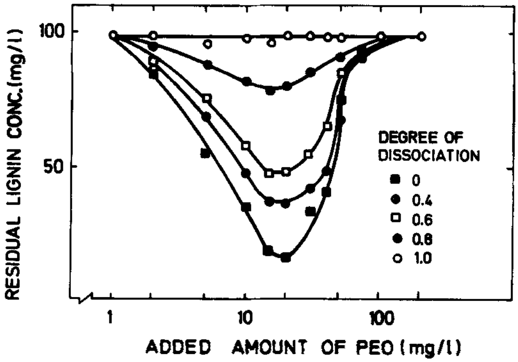

FIG. 2. The effect of PEO on lignin removal at different degrees of dissociation (α) of the lignin sol. pH 4.8 to 6.2.

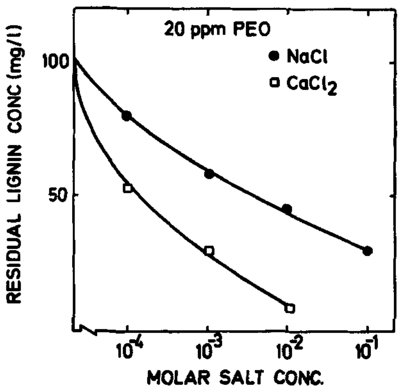

FIG. 3. The effect of NaCl and $CaCl_2$ on lignin removal. Added amount of PEO = 20 mg/l. $\alpha = 1$, pH 6.2.

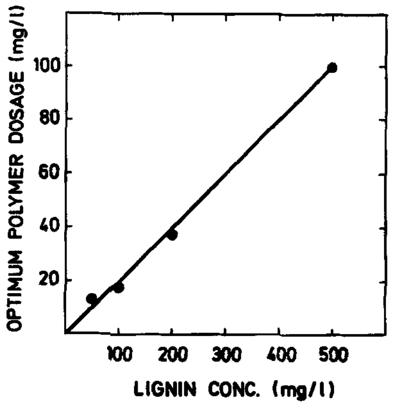

FIG. 4. The effect of lignin sol concentration on the O.P.D. $\alpha = 0$, pH 4.8.

strongly on the valency of the counterion. The critical coagulation concentration for a lignin sol at this pH in the absence of PEO is 0.4 *M* NaCl and 6×10^{-3} *M* $CaCl_2$ (*6*). Thus protonization of the carboxylic groups is not a necessary condition for flocculation of a lignin sol with PEO.

Experiments were also performed in which the lignin concentration was varied from 50 to 500 mg/l (pH 4.8, $\alpha = 0$). As shown in Fig. 4, a linear relationship between the O.P.D. and the lignin concentration was obtained. This result indicates complete adsorption of PEO onto the lignin sol at the O.P.D. at this pH. It is well known that PEO forms association compounds with polycarboxylic acids (*7*, *8*), due primarily to hydrogen bond formation between the carboxylic groups and the ether oxygens on the PEO chain.

In order to gain further insight into the role of the carboxyl groups, the PEO adsorption was measured at the O.P.D. with both protonized lignin sols ($\alpha = 0$) and deprotonized lignin sols ($\alpha = 1$).

In order to measure the concentration of the PEO left in solution, 0.5 *M* NaCl had to be added to the sol in order to flocculate it (lignin concentration, 100 mg/l; PEO concentration, 20 mg/l). The results show that less than 2 % of the PEO was left in solution in the case of the protonized sol, and 9 % of the PEO was left in solution in the case of the deprotonized sol. Although adsorption seems to be slightly affected by dissociation of the carboxylic groups, this group is thus considered to be of minor importance for the adsorption mechanism in this case.

At high PEO dosages, the lignin sols become restabilized due to the protective action of the PEO chains. These sols are enthalpically stabilized and are flocculated when heated. The C.F.T.'s of the sols were monitored in the presence of different electrolytes at electrolyte levels so high that the electrostatic interaction between the particles could be neglected.

Figure 5 shows that the C.F.T. is identical with the θ-temperature for the PEO. The C.F.T. was independent of PEO dosages exceeding 80 mg/l

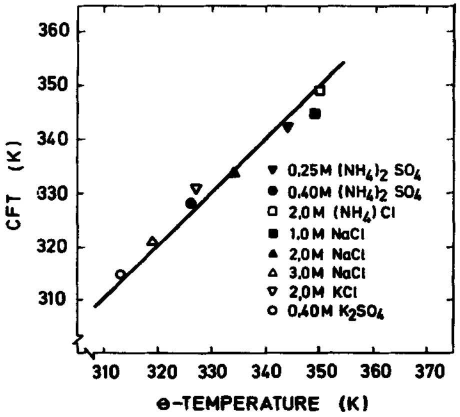

FIG. 5. Correlation between C.F.T. and the θ-temperature of PEO. Data on θ-temperature (determined from cloud-point curves) taken from Ref. *24*. Lignin sol concentration = 100 mg/l. Added amount of PEO = 100 mg/l. $\alpha = 0$, pH 4.8.

(lignin sol concentration, 100 mg/l). Flocculation was not found to be fully thermally reversible.

DISCUSSION

The results presented in this paper are best understood in terms of current concepts of bridging flocculation by nonionic polymers (*10–12*). For effective interparticle bridging to occur, at least two conditions must prevail. First, the polymer must be adsorbed onto the particle surface. The adsorption experiments on the lignin sol at different degrees of dissociation and the flocculation experiments with simple electrolytes at full dissociation strongly suggest that complex formation involving the carboxyl group is of minor importance.

It is also well known that PEO forms association compounds with a wide variety of phenols and phenolic resins (*3*). This suggests that phenolic groups are the primary adsorption sites for PEO.

The second condition for effective bridging flocculation is that the particles must be able to approach each other sufficiently closely for the high polymer to be capable of forming bridges between the particles. The distance of closest approach between different particles is limited by the thickness of the electrostatic double layer. As long as the double layer repulsion between different particles is high enough, the sol remains stable, although polymer is adsorbed to the particle surface.

The role of the simple electrolytes is thus to reduce the double layer thickness outside the polymeric layer on the particle surface. Thus the electrolyte concentration needed to cause flocculation (sensitization flocculation) is much less than the amount of electrolyte needed for coagulation in the absence of polymer, because in the latter case the electrostatic repulsion has to vanish at much smaller interparticle distances.

The greater effectiveness of the divalent counterion in causing sensitization is due to its greater ability to compress the electrostatic double layer and reduce the surface charge by specific adsorption on the particle surface.

The lack of a certain critical amount of electrolyte needed to sensitize the flocculation reaction can be explained at least in part by a wide distribution in molecular weight of the PEO sample. For polymers with a narrower molecular weight distribution (PVaC), it has been found that a certain critical amount of electrolyte is needed to induce flocculation of AgI sols (*11*). The role of the heterodisperse particle size and shape is naturally difficult to assess, but it should be noted that the critical electrolyte concentration for coagulation of this lignin sol is very well defined.

The effect of pH was similar to that of the influence of simple electrolytes on the flocculation behavior. Decreasing the Stern potential of the lignin sol by protonization decreases the thickness of the electrostatic double layer, thereby allowing the polymer to bridge between different particles.

When the degree of dissociation of the lignin sol is decreased, aggregation between the unit particles takes place, presumably due to hydrogen bond formation between the carboxylic groups and phenolic groups (*2*). Thus the sol is in a more aggregated state before polymer addition although the sol exhibits long-term stability. However, this factor is probably of minor importance since thermal aging of the sol, which increases the extent of aggregation (*2*), was found not to affect the O.P.D. for a fully protonized lignin sol. Flocculation of the sol in the absence of an electrolyte is usually referred to as adsorption flocculation (*12*), although in this case the distinction is only a semantic one as the mechanism of flocculation is considered to be essentially identical with and without a simple electrolyte.

In order to achieve a visual perception of the flocculation and stabilization process, the following approximate analysis can be made.

The size of the polymer in solution can be estimated with the aid of the K value in the Mark-Houwink equation and the Flory-Fox relationship (*12*). Taking K as 1.25×10^{-4} (*14*) and Φ as 2.0×10^{21} (*13*), the root-mean-square end-to-end distance of the PEO polymer chain ($M_w = 4 \times 10^6$) in the unpertubed state can be calculated to be 780 Å. This value may be compared with the size of the sol particles (*2*) which are of the order of 200 Å ($\alpha = 1$) to $\sim 10^4$ Å ($\alpha = 0$).

The stabilization of the sol particles is easily understood in terms of current theories of steric stabilization (*13*, *15*–17). If a particle surface is covered with a polymer layer protruding out in solution, the motion of the polymer segments prevents the particles from sticking together. The polymer layer on the particle surface acts as a steric barrier toward aggregation. In this type of stabilization the solvency of the adsorbed polymer on the particle is the prime factor responsible for the stability of the dispersion. It can be shown that the free energy during interpenetration of the polymeric chains can be written as (*13*, *17*)

$$\Delta G_M = \psi_1\left(1 - \frac{\theta}{T}\right) \times (\text{geometric term})$$

where ψ_1 is an entropy parameter, T is the absolute temperature, and θ is the θ-temperature of the polymer. ΔG_M is positive for stable dispersions and negative for instable dispersions. The dispersions that flocculate on heating are said to be enthalpically stabilized. Dispersions stabilized by PEO are known to be enthalpically stabilized (*17*).

The close relationship between the θ-temperature of the polymer and the critical flocculation temperature of dispersions with a stabilizing polymer anchored to the particle surface has also been demonstrated in a number of cases (*17–22*).

Steric stabilization occurs when the surface is completely or almost completely covered with polymer (*18*, *23*). Thus the stability or instability of the dispersion is dependent on neither particle size (*23*) nor polymer molecular weight (*21*, *23*) (above a certain molecular weight). This means that the theory is readily applicable to sols with a broad distribution of particle sizes and shapes. The inherent assumption in applying the theory to polymers not covalently anchored to the surface is that displacement of the polymer from the surface does not occur before the θ-temperature is reached.

The data in Fig. 5 illustrate the application of this theory to practical systems.

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