Controlled Black Liquor Viscosity Reduction through Salting-in

Joanna E. Roberts and Saad A. Khan
Dept. of Chemical Engineering, North Carolina State University, Raleigh, NC 27695
Richard J. Spontak
Dept. of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695

Black liquor viscosity increases exponentially with solids content and therefore causes processing problems for the paper industry by being a limiting factor in the Kraft pulp process. This study investigates a new approach for achieving viscosity reduction by "salting-in" black liquor through the addition of thiocyanate salts. These salts generally increase the solubility of the polymer constituents in black liquor, leading to a decrease in its viscosity. Several thiocyanate salts capable of reducing liquor viscosity by more than two orders of magnitude have been identified, with viscosity reduction greatest at high solids content. Salting-in of black liquor depends on the cation paired with the thiocyanate anion, as well as on solution pH and temperature. Comparative studies reveal that GuSCN is the most effective viscosity-reducing agent of the series examined and that lignin plays an important role in the viscosity behavior of both unmodified and salted-in black liquor at high solids concentrations. These experimental findings are interpreted in terms of the underlying principles that describe salting-in and how it affects aqueous solution structure.

Introduction

The most common process used to produce pulp and paper is the Kraft process (Gierer, 1980). In this operation, wood chips and various chemicals (e.g., NaOH and Na_2S), collectively known as *white liquor*, are cooked in a digester to produce pulp and a complex residual filtrate, referred to as *black liquor* due to its dark color. For this process to be cost-effective, the cooking chemicals that react with the wood chips and subsequently contribute to the production of black liquor must be recovered (Smook, 1992). In order to regenerate these chemicals, black liquor is subjected to several environmentally deleterious and energy-intensive treatments such as evaporation and burning. Rising energy costs and strict environmental regulations dictate that black liquor must be combusted at the highest possible solids concentration (Soderhjelm, 1986). Processing black liquor at high solids content greatly enhances the energy efficiency of the Kraft process (Boone, 1991) and reduces SO_2 emissions (Ryham and Nikkanen, 1992). The ultimate concentration of black liquor, however, is limited in practice by rheological considerations, since black liquor exhibits an exponential increase in viscosity as its solids content rises (Ramamurthy et al., 1992). Higher liquor viscosity consequently hinders processability in terms of transport, storage, and handling.

Black liquor is a complex aqueous solution composed of several components, including lignin, polysaccharides, and salts (see, for example, Table 1). Previous studies of black liquor have yielded conflicting results regarding the role of each of these components in the viscosity rise. Recent efforts have demonstrated that both the lignin (Small and Fricke, 1985) and polysaccharide (Soderhjelm, 1989) fractions may be responsible for the exponential increase in black liquor viscosity. While strong (or concentrated) black liquor is a sticky, unpumpable liquid (Boone, 1991; Ramamurthy et al., 1992), even less concentrated (more pumpable) liquor can induce processing complications, such as pluggage and scaling in the recovery boiler (Ryham and Nikkanen, 1992). To prevent such problems, methods such as heat treatment (Soderhjelm, 1986; Ryham, 1992; Soderhjelm, 1988) and oxidation (Milanova and Dorris, 1990; Frederick and Adams, 1992) have been developed and are currently employed to reduce the viscosity of black liquor so that a higher solids content can be obtained. In the heat-treatment process, liquor

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Correspondence concerning this article should be addressed to S. A. Khan.

Table 1. Typical Composition of Black Liquor*

Lignin	30–34
Polysaccharides	2–3
Aliphatic Acids	31–32
NaHS	4
NaOH	1.5–2.5
Na_2SO_4	3–4
Na_2CO_3	7
NaCl	1
Na bound to organics	12
$Na_2S_2O_3$, Na_2SO_3, Na_2S_X	0.5
K_2CO_3	2
S in lignin	1.5

Source: Reproduced with permission from Soderhjelm (1989).
*By wt. % dry solids

is removed from multiple-effect evaporators and heated at an elevated temperature for an extended period of time (e.g., 140°C for 2 h) (Soderhjelm, 1988). This procedure results in an irreversible decrease in viscosity due to depolymerization of polymer chains present in the liquor (Ryham and Nikkanen, 1992). In the oxidation process, black liquor is exposed to air to convert sulfides to thiosulfate (Milanova and Dorris, 1990), thereby decreasing viscosity through a reduction in residual alkali concentration. However, this viscosity decrease is reversible; that is, addition of alkali following the oxidation step returns the liquor to its original viscosity.

While heat treatment and oxidation are used in commercial mills, they are accompanied by significant disadvantages. They may even induce a viscosity increase if the black liquor possesses an initially low residual alkali concentration (Frederick and Adams, 1992). Both processes are also cost-intensive and may not be economically viable in terms of the service they provide. Heat treatment, for instance, requires additional energy to raise the temperature of the liquor. Similarly, oxidation rids the liquor of its fuel value (Smook, 1992), which translates into higher energy input. It is therefore necessary to develop a more economical procedure for reducing the viscosity of black liquor to obtain a processable, high-solids liquid. In this article we present an alternative approach based on the concept of *salting-in* to achieve this objective. Although salting-in has been recognized for many years and has been employed in applications such as cloud-point manipulation (Luck, 1980), its effectiveness in modifying the rheological behavior of complex aqueous solutions such as black liquor has never been fully examined. Malmsten and Lindman (1992), for example, have reported that upon addition of NaSCN salt, the stability regime of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer gels in aqueous media can be controllably shifted to higher copolymer concentration and temperatures. Likewise, Prevysh et al. (1995, 1996a) have demonstrated that addition of various thiocyanate (SCN^-) salts to lyotropic hydroxypropylcellulose (HPC) solutions results in a slight shift of the isotropic → mesophase transition to higher HPC concentration, as well as a systematic reduction in the dynamic elastic modulus (G') with increasing salt or HPC concentrations. These observations suggest that the presence of SCN^- salts in aqueous solutions containing organized polymeric assemblies disrupts or swells existing microstructure, and are consistent with results obtained by salting-in hydrogen-bonded interpolymer complexes (Prevysh et al., 1996b).

Using this novel approach to tailor the property-controlling microstructure of black liquor, we report that addition of thiocyanate (SCN^-) salts permits control and reduction of black-liquor viscosity by more than two orders of magnitude in some cases. We have found that the salting-in mechanism is dependent on several factors, including temperature, pH, black-liquor solids concentration, and the cation paired with the thiocyanate anion. Experimental findings are interpreted in terms of the underlying principles that describe salting-in and aqueous solution structure to explain the possible microstructural reasons for these promising results.

Structure of Aqueous Polymer Systems and Salting-in/Out

In aqueous polymer solutions, such as black liquor, complex interactions between water, macromolecules, and salts play a crucial role in the development of process-controlling rheological properties. The solubility and self-assembly of the solutes, which are directly related to black-liquor viscosity, depend strongly on solute–water interactions, salt-induced ionic interactions, and (poly)electrolytic repulsive electrostatic interactions (Scopes, 1987; Mandel, 1983). An understanding of the molecular structure of water is therefore a prerequisite for the manipulation of complicated water-solute interactions. Although the exact nature of water remains unknown, the following description is widely accepted.

Liquid water, like ice, exhibits a tetrahedral arrangement of hydrogen-bonded molecules. In contrast to ice, however, water possesses a less ordered structure with numerous lattice vacancies (Mikhailov and Syrnikov, 1960). Water molecules are therefore free to diffuse and fill unoccupied spaces that evolve, since the structure of water constantly changes due to hydrogen bonding and debonding. Hydrogen bonds are cooperative on the molecular scale, and formation of a single hydrogen bond propagates the formation of several bonds. Similarly, when one hydrogen bond breaks, several simultaneously break. These cooperative groups of hydrogen bonds have been referred to by Frank and Wen (1957) as "flickering clusters" because they continually form and break apart within water. When a nonpolar solute dissolves in water, a more highly ordered structure called an *iceberg* forms within a cluster. In an iceberg, water molecules surround nonpolar regions, resulting in an effective reduction in entropy (Frank and Evans, 1945).

Addition of salt ions to an aqueous polymer solution typically reduces the number of free water molecules available to hydrate the polymer chains. The solubility of dissolved polymer is greatly decreased, whereas the solution viscosity is increased (Conway, 1981). This effect, known as *salting-out*, occurs because the salt ions create ionic fields that polarize surrounding water molecules. The water molecules are then attracted toward the ions, effectively isolating the less polarizable polymer chains (Conway, 1981). In aqueous polymer solutions, more salt-induced water–water hydrogen bonds form, whereas the number of water–polymer interactions required for solubility is diminished. Salting-out therefore decreases polymer solubility, eventually leading to precipitation (Scopes, 1987; Melander and Horvath, 1977). Figure 1 depicts this effect in which the salt serves as a water "structure maker" (Luck, 1980) by facilitating the formation of iceberg structures.

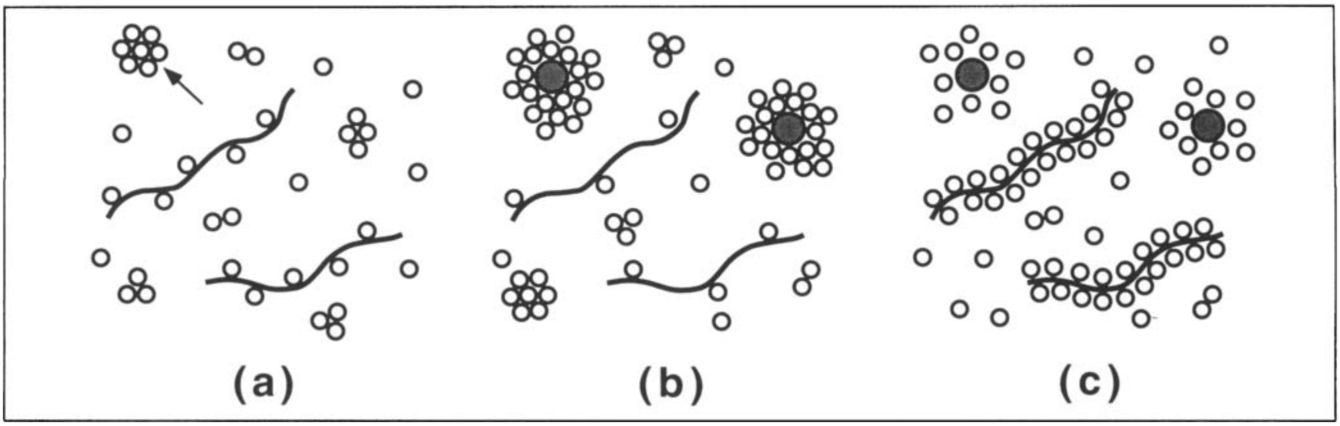

Figure 1. Mechanisms that occur on addition of salts to a dilute aqueous polymer solution.

In the absence of salt (a), the solution consists of free water molecules (○), flickering water clusters (arrow), and polymer chains (solid lines). If the added salt (shaded circle) induces *salting-out* (b), polymer–water interactions are reduced, eventually bringing about polymer precipitation. If the salt is a "structure-breaker" (c), *salting-in* occurs, in which case polymer–water interactions are enhanced and polymer solubility increases.

In contrast, some large and weakly polarizing ions have the opposite effect in water (Luck, 1980; Balzer, 1993). These ions are referred to as *structure breakers* (Luck, 1980) because they hinder the formation of water clusters. This phenomenon, also illustrated in Figure 1, is known as *salting-in*. The reduction of water–water hydrogen bonds liberates water molecules, thereby promoting more water–polymer interactions and increasing polymer solubility.

The effects just described refer to addition of neutral salts to an aqueous solution. An acidic or basic salt is expected to alter the pH of the solution (Scopes, 1987), thus changing the magnitude of interactions between water and solute species (von Hippel and Schleich, 1969a). This point must be carefully considered in the case of Kraft lignin, which self-associates and, as Lindstrom (1979) points out, precipitates from solution upon a reduction in pH.

Since the goal of this research is to enhance black-liquor processing through tailored viscosity reduction, addition of a structure-breaking salt to increase polymer solubility appears commercially attractive (Spontak et al., 1995). Increased solubility should reduce black-liquor viscosity and eliminate the problems traditionally associated with high-solids handling. One anion that has been shown to exhibit pronounced salting-in behavior is thiocyanate (SCN^-) (Luck, 1980; Robb, 1983). In this study, five cations have been paired with the SCN^- anion to identify the most effective salt for black-liquor viscosity reduction. The cations selected here are guanidine (Gu^+), ammonium (NH_4^+), sodium (Na^+), potassium (K^+), and lithium (Li^+).

Experimental Methods and Materials

Commercial black liquors obtained from a pulp mill in the southern United States were used in this study. Experiments were conducted using 80/20 (wt. %) softwood/hardwood liquor samples that were obtained following tall oil extraction at a solids concentration of 62 wt. %. Solutions possessing higher solids concentrations were prepared by first heating approximately 350 mL of the pulp mill liquor for different times in an open container. These solutions were continuously stirred at temperatures not exceeding 90°C. A small, preweighed portion of each sample was then dried in an oven at 100°C for 48 h, and weighed again to determine its solid content. Since black-liquor viscosity may vary considerably between batches (Soderhjelm, 1986), samples at different solids concentrations were prepared from the same master batch to eliminate such variation.

A dry sample of Indulin A lignin was obtained from Westvaco (Charleston, SC). Model lignin solutions were prepared by dissolving sodium hydroxide (NaOH) and lignin in distilled water. Samples were stirred at ambient temperature until complete lignin dissolution was achieved. When necessary, the pH of each solution was adjusted to above 12 by the addition of NaOH pellets. High-solids solutions were obtained through the same evaporation procedure described earlier for black liquor.

Salt-modified black-liquor and lignin solutions were prepared by adding predetermined quantities of SCN^- salt crystals to already concentrated liquor samples. The mixtures, covered to avoid premature water evaporation, were then stirred vigorously and heated at approximately 40°C for 30 min to promote salt dissolution. Control samples were subjected to identical treatment to ensure comparable thermal history (needed for quantitative analysis).

A Rheometrics Dynamic Stress Rheometer (DSR II) with a 25-mm parallel-plate geometry and a 1-mm gap was used to measure rheological properties of these virgin and salt-modified black-liquor solutions. All experiments were conducted at 25 or 60°C with titanium-coated tools capable of withstanding the elevated pH of black liquor ($\approx 12-14$). Both steady shear and dynamic oscillatory shear experiments were performed to obtain the steady shear viscosity (η) and the dynamic elastic modulus (G'), respectively, of various samples. In addition, bright-field light micrographs were obtained for several samples using a Nikon Optiphot light microscope.

Results and Discussion

Novel approach to black-liquor viscosity reduction

The effect of adding ammonium thiocyanate (NH_4SCN) salt on the viscosity (η) of commercial black liquors with different solids concentrations is displayed in Figure 2. It is clear from this figure that 0.6 M of added salt significantly retards

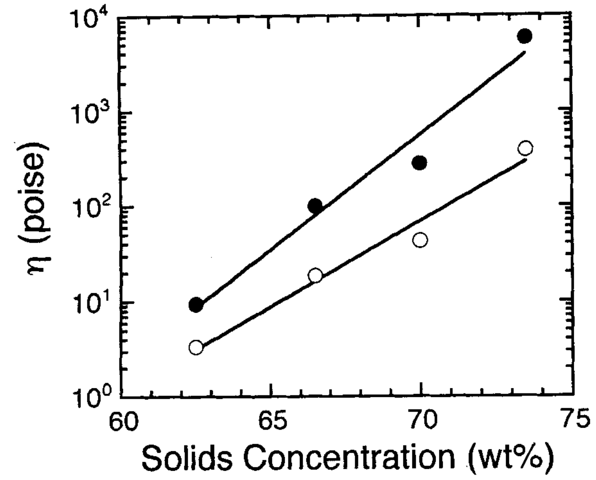

Figure 2. Dependence of viscosity on solids concentration (excluding added salt) in black liquor solutions containing no (●) and 0.6 M (○) NH_4SCN.

the increase of black-liquor viscosity, especially at high-solids content. This trend indicates that salt-containing liquor could be evaporated to a higher solids content without extensive energy consumption or associated processing problems. While the data in Figure 2 correspond to solutions in which salt is added *after* liquor concentration, results obtained from samples prepared by adding salt prior to liquor concentration show comparable viscosity reduction. It is also important to note that the black-liquor solutions employed throughout this study were found to be Newtonian unless otherwise noted. In the latter case, viscosities from the Newtonian plateau region are used for comparative purposes.

While Figure 2 demonstrates that the addition of 0.6 M NH_4SCN substantially decreases the viscosity of black liquor over a broad solids range, the relative efficacy of salting-in is strongly dependent upon the concentration of salt added. In Figure 3, this effect is shown for guanidine thiocyanate (GuSCN). Normalized viscosities ($\eta_r = \eta/\eta_o$, where η is the viscosity of the sample and η_o is the viscosity of the virgin liquor at the same solids concentration) are shown for three black-liquor samples of different solids concentrations (62, 67 and 76 wt. %). Corresponding values of η_o are equal to 11.0, 200, and 1×10^4 Pa·s, respectively. Note that without GuSCN salt, the 76 wt. % solids solution possesses the highest viscosity of this series. Values of η_r from all three black-liquor samples exhibit a substantial decrease with increasing salt concentration, supporting the idea that SCN^- ions break the structure of water and salt-in the polymeric components of black liquor.

Close examination of Figure 3 reveals that addition of salt to a more concentrated liquor yields a more pronounced effect on measured viscosity. The viscosity of the 76 wt. % solids black liquor, for instance, decreases by more than two orders of magnitude with 1 M GuSCN, whereas the viscosity of the 62 wt. % solids sample is reduced by a factor of only ~8. With less water present in a concentrated liquor solution, the salt may have a more noticeable effect because a larger number of salt molecules are present per water cluster. In this case, more water structures may be broken, reducing the viscosity more dramatically than in a lower solids content liquor.

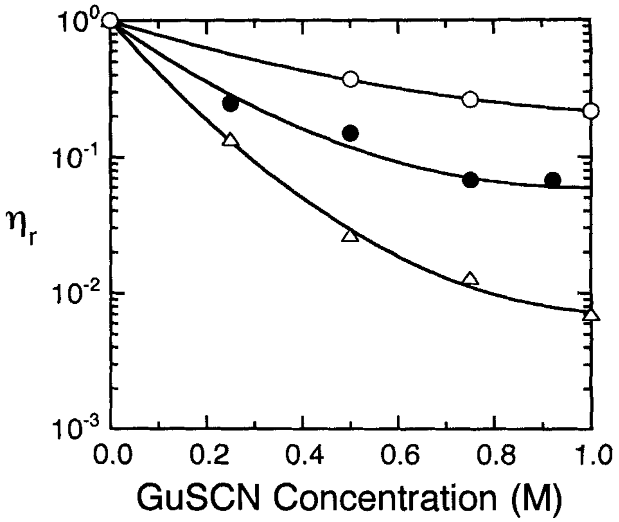

Figure 3. Viscosity normalized with respect to untreated black liquor (η_r) as a function of added GuSCN for three solids concentrations (in wt. %): 62 (○), 67 (●), and 76 (△).

Effect of temperature on salting-in

Because many pulp and paper mills transport and store black liquor at temperatures above 25°C, the effect of elevated temperature on salted-in black-liquor viscosity is of considerable importance. Figure 4 displays the effect of temperature at 25°C and 60°C on the magnitude of salted-in liquor viscosity with GuSCN and NaSCN. To facilitate data comparison at different temperatures, reduced viscosity is presented as a function of salt concentration for liquors containing 76 wt. % solids.

As seen in Figure 4, the magnitude of viscosity reduction due to salting-in is lessened by almost an order of magnitude

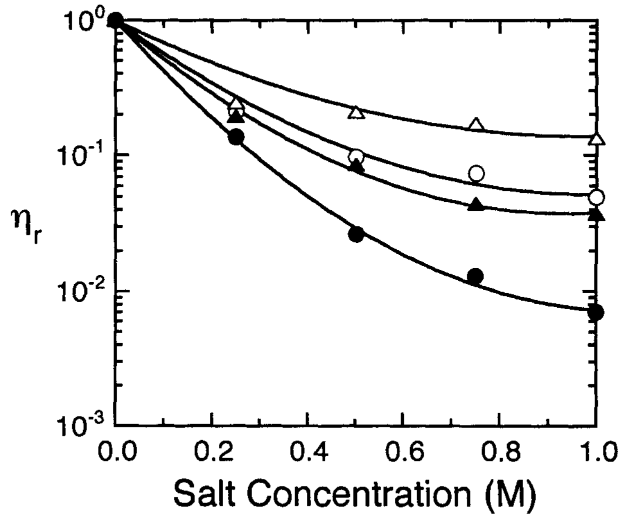

Figure 4. Variation of η_r with salt concentration for two salts (NaSCN, open symbols; GuSCN, closed symbols) at 25°C (circles) and 60°C (triangles) (the black liquor solids concentration is 76 wt. %).

when the temperature is raised from 25°C to 60°C. This observation most likely occurs because the ability of the large SCN^- anions to break the hydrogen-bonded structure of water (flickering clusters) is weakened at elevated temperatures (Luck, 1980). At 60°C, fewer water structures are available to be disrupted by the SCN^- anions. Figure 4 also demonstrates that the viscosity-reduction capability of GuSCN and NaSCN both decrease by almost the same extent as the temperature is increased from 25°C to 60°C. This observation, in accord with aqueous solution behavior, suggests that an increase in temperature primarily affects the hydrogen-bonded structure of water (Israelachvili, 1992). The effect of temperature on salt-induced viscosity reduction therefore should be nearly independent of the salt employed.

Although viscosity reduction is clearly less at 60°C than at 25°C for both salts shown in Figure 4, it is still significant. At 60°C and 1 M salt concentration, GuSCN is responsible for reducing black-liquor viscosity by more than one order of magnitude, while NaSCN reduces liquor viscosity by a factor of 8. These results suggest that if this technology is to be commercially implemented, paper mills would need to adjust their processing temperature to achieve a maximal viscosity reduction for a given salt concentration (Roberts et al., 1996).

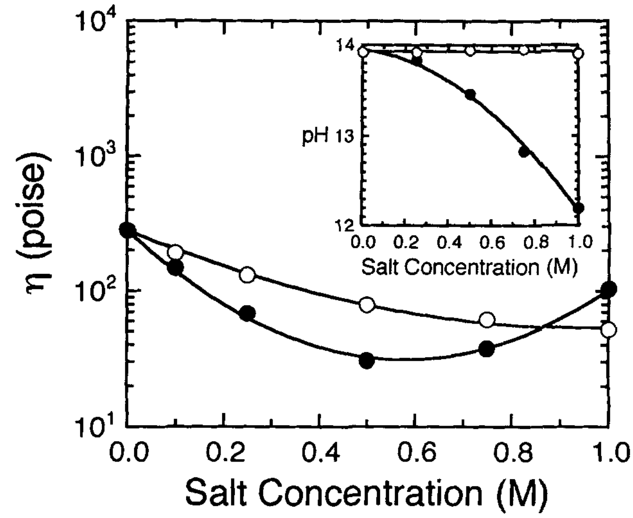

Figure 5. **Viscosity as a function of salt concentration in black liquor solutions (69 wt. % solids) containing NaSCN (○) and NH_4SCN (●) (the pH of each solution is shown in the inset).**

Neutral vs. acidic salt additives

Kraft lignin possesses a significant number of negatively charged phenolic and carboxylic acid groups at high pH (MacDonald, 1969). However, as the pH of the solution drops, the charges begin to neutralize and the lignin molecules self-associate (Lindstrom, 1979). Due to this effect, several previous viscosity-reduction techniques yield an increase in viscosity when the black-liquor residual alkali is decreased below a critical level (Frederick and Adams, 1992). These results suggest that a change in black liquor pH may affect the magnitude of salt-induced viscosity reduction. This possibility is explored in Figure 5, which illustrates the effects of added NH_4SCN and NaSCN on black-liquor viscosity. Both salts promote a decrease in black-liquor viscosity with increasing salt concentration up to a salt concentration of 0.50 M. Above 0.50 M, further addition of NaSCN continues to decrease black-liquor viscosity, whereas additional NH_4SCN salt causes a noticeable increase in viscosity. This anomalous viscosity increase can be explained in terms of pH considerations (Roberts et al., 1996).

Addition of NH_4^+ cations to an aqueous solution results in the following chemical reaction:

$$NH_4^+\ (aq) + H_2O\ (l) \Leftrightarrow H_3O^+ (aq) + NH_3\ (aq).$$

According to Atkins (1989), the solution of weak base (NH_3) and its conjugate acid (NH_4^+) will act as a buffer, stabilizing near a pH equal to the pK_a of the conjugate acid (pH ~ 9.25) (Atkins, 1989). Therefore, adding NH_4^+ ions to a basic aqueous solution like black liquor should result in a decrease in liquor pH. The inset in Figure 5 compares the change in black liquor pH upon addition of a neutral salt (NaSCN) and an acidic salt (NH_4SCN). Consistent with the concepts and observations discussed earlier, NH_4SCN promotes a considerable reduction in black liquor pH, whereas addition of neutral NaSCN molecules results in minimal effects on black liquor pH. Thus, in the case of NH_4SCN, the upturn in viscosity can be attributed to a reduction in pH, suggesting that an optimal salt concentration exists for maximum viscosity reduction.

In order to better understand the upturn in black-liquor viscosity observed with NH_4SCN at concentrations above 0.50 M, the elastic modulus (G') of a control black liquor (62 wt. % solids) is compared in Figure 6 with that of a liquor containing 1 M NH_4SCN salt. This figure shows the frequency dependence of G', which is sensitive to and can provide insight into microstructural formation. In the control black liquor, G' increases with frequency (ω) and scales as ω^2, a behavior characteristic of viscous liquids with no established microstructure (Ferry, 1980; Prud'homme, 1990). For the sample containing 1 M NH_4SCN salt, however, G' is slightly

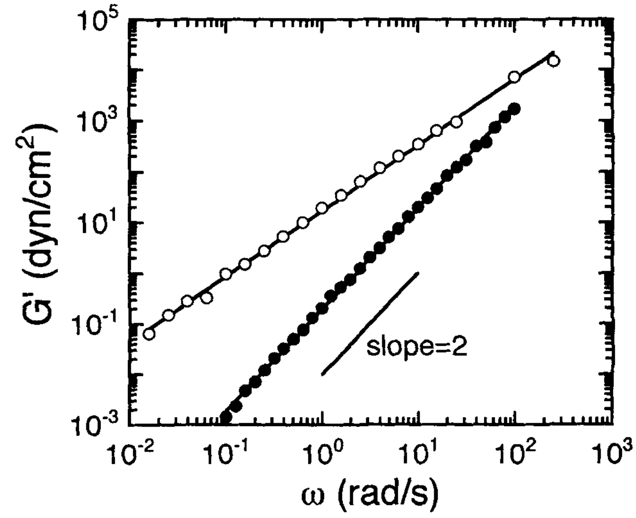

Figure 6. **Dependence of the dynamic elastic modulus (G') on frequency (ω) for black liquor solutions (62 wt. % solids) containing no (●) and 1 M (○) NH_4SCN; also displayed is the limiting slope of concentrated polymer solutions.**

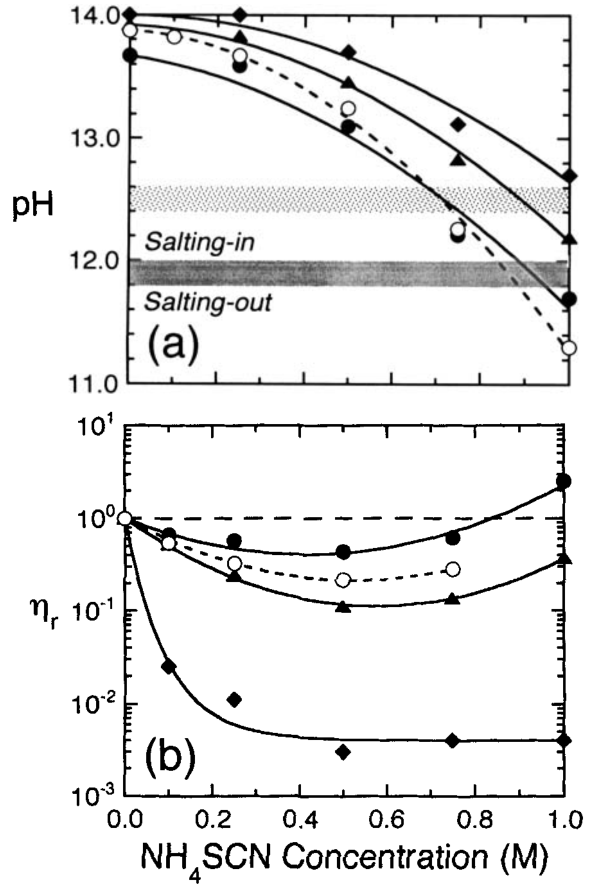

Figure 7. Effect of added NH$_4$SCN salt on (a) pH and (b) η_r for black liquor solutions with solids concentrations (in wt. %) of 62 (●), 67 (▲) and 73 (◆), and a model lignin solution (○) with 63 wt. % solids.

The shaded regions in (b) identify the pH ranges over which salting-in either becomes less effective (lightly shaded) or eventually yields to salting-out (heavily shaded).

larger and possesses a lower slope with respect to ω. This change in G' reveals that addition of excess salt to black liquor results in the formation of microstructure. It is feasible that microstructural formation in black-liquor solutions with NH$_4$SCN concentrations above 0.75 M reflects association of lignin molecules due to a NH$_4^+$-induced reduction in black liquor pH.

To further ascertain the roles of both pH and lignin on salting-in behavior, NH$_4$SCN salt was added to a model lignin solution, as well as to three black liquor solutions of differing solids concentrations. The anticipated decrease in solution pH with NH$_4$SCN addition is seen in Figure 7a for the four samples. Reduced viscosities (η_r) for the same four samples in Figure 7a are displayed in Figure 7b. At high NH$_4$SCN concentrations in both black liquor and lignin, a viscosity upturn is evident, in some cases approaching (69 wt. % solids black liquor and 63 wt. % solids lignin) or exceeding (62 wt. % solids black liquor) unity, which corresponds to the viscosity of the initial, unsalted solution. Comparison of the data in Figures 7a and 7b reveals that, when the black liquor or lignin solution pH is forced below the lightly shaded region shown in Figure 7a, the viscosity no longer decreases monotonically with salt addition, but instead begins to rise. In this regime, though, the viscosity of the salt-treated liquor remains below that of the original virgin sample. As more NH$_4$SCN salt is added and the pH decreases below the heavily shaded region in Figure 7a, the viscosity of the black-liquor solution exceeds that of the unsalted liquor, and salting-out rather than salting-in occurs.

If enough NH$_4$SCN is added to a lignin solution and the pH drops below the heavily shaded region shown in Figure 7a, salting-out can result in phase separation between water and lignin molecules. Shown in Figure 8 are a pair of bright-field light micrographs of two 55 wt. % lignin solutions, one containing no NH$_4$SCN salt and one with 1 M NH$_4$SCN. The micrographs in Figure 8a demonstrate that in the control sample, the solution remains macroscopically homogeneous (i.e., one phase). If 1 M NH$_4$SCN salt is added, macroscopic phase separation between water and lignin results, as is evident in Figure 8b. Thus, salting-out may not only increase solution viscosity, but may also affect solution stability by promoting phase separation.

The results obtained for Kraft lignin solutions (Figure 7) are comparable to those obtained for black liquor and sug-

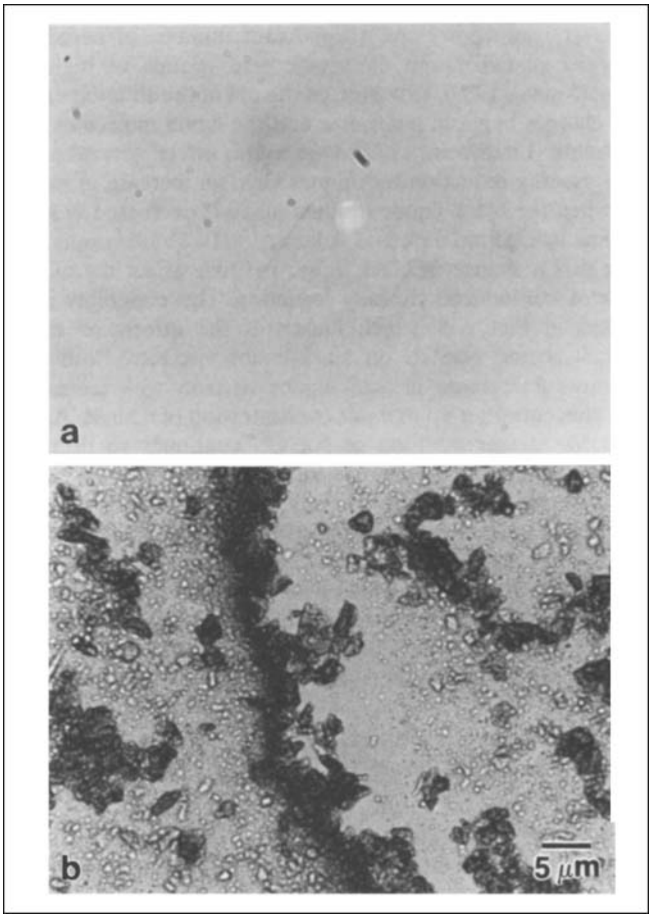

Figure 8. Bright-field light micrographs of 55 wt. % lignin solutions in the presence of (a) no salt and (b) 1 M NH$_4$SCN.

Salting-out at high NH$_4$SCN concentrations and reduced pH (Figure 7) results in macroscopic phase separation between water and lignin (opaque regions).

gest that Kraft lignin is a primary component responsible for viscosity changes with pH. These data, in conjunction with those provided in Figure 6, support the findings of Lindstrom (1979) that below a critical pH, Kraft lignin molecules lose their charges and consequently self-associate. With the formation of microstructure in solution, the viscosity of black liquor should increase, rather than decrease, in which case black-liquor viscosity reduction through salting-in can no longer be achieved. These results suggest that use of an acidic salt (e.g., NH_4SCN) as a water-structure breaker requires a solution pH above the heavily shaded region shown in Figure 7a ($pH > 11.8-12.0$) to achieve the desired reduction in black-liquor viscosity.

Effect of cation on salting-in

The order in which ions alter water structure follows the Hofmeister, or lyotropic ion, series and is related to the size and hydration of ions (Luck, 1980; Edsall and Wyman, 1958). Since anions dominate the salting-in/out effect, their position in the series dictates performance (Robb, 1983). The position of the cation does, however, play a role in the lyotropic effect of a salt. According to von Hippel and Schleich (1969b), the effects of the anion and cation are additive, and coupling a structure-breaking cation with a structure-breaking anion increases the destabilizing capability of the anion. To determine the most effective SCN^- salt for black-liquor viscosity reduction, we have examined several different thiocyanate salts.

Because it was demonstrated in the previous section that acidic salts may effect the pH of black liquor, only neutral salts are considered in the present comparison. In the absence of significant pH changes, the effect of *cation* on the magnitude of SCN^--induced viscosity reduction should be isolated. While most of the salts examined in this section are neutral (i.e., they do not donate/accept protons from other species in solution), the guanidine cation (Gu^+), in the strictest sense, is not. Its conjugate, guanidine (Gu), however, is a strong base, and the Gu^+ cation behaves as a *very* weak acid in solution (von Hippel and Schleich, 1969a). Therefore, the Gu^+ cation results in only minimal changes in solution pH when added to black liquor, and for the purposes of this investigation will be considered effectively neutral.

The change in viscosity due to salting-in, with respect to cation, is provided in Figure 9 for a series of four SCN^- salts: lithium thiocyanate (LiSCN), sodium thiocyanate (NaSCN), potassium thiocyanate (KSCN), and guanidine thiocyanate (GuSCN). All measurements have been obtained using a 76 wt. % solids black-liquor solution and a 51 wt. % solids model Kraft lignin solution. Of the four salts, GuSCN clearly yields the largest viscosity reduction of the series in both the lignin and black-liquor solutions, followed by KSCN. In black liquor, the ability of NaSCN to reduce viscosity is less than that of KSCN, with LiSCN being the least effective structure-breaking salt. In contrast to this apparent difference between salt efficacy in black liquor, the NaSCN, KSCN, and LiSCN salts exhibit comparable viscosity reduction in the Kraft lignin solution at low salt concentrations. At higher salt concentrations, however, the cation trend observed in black-liquor solutions is again manifested.

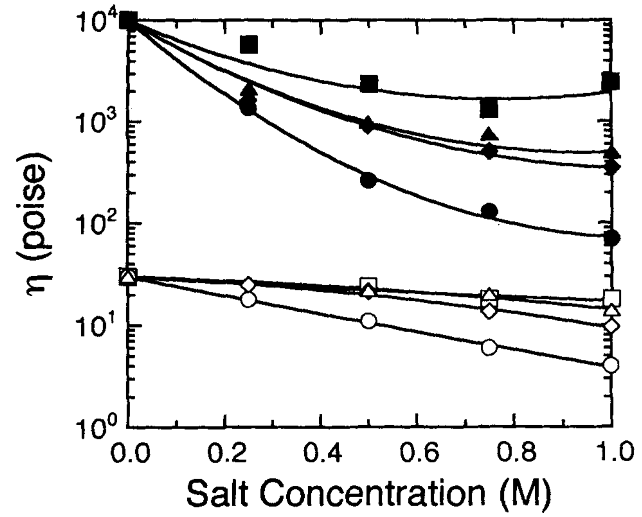

Figure 9. Dependence of viscosity on salt concentration illustrating the efficacy of four salts.

(GuSCN, circles; KSCN, diamonds; NaSCN, triangles; LiSCN, squares) in black liquor (filled symbols) and lignin (open symbols) solutions containing 76 and 51 wt. % solids, respectively.

The efficiency of salting-in can be qualitatively predicted from cationic radius considerations. The cation with the smallest ionic radius (Li^+) possesses the least structure-breaking ability, while the cation with the largest radius (Gu^+) promotes the greatest viscosity reduction. This trend is consistent with previous results indicating that large, less polarizable ions yield the greatest salting-in effect (Luck, 1980; Balzer, 1993). Large cations may also be more effective in conjunction with SCN^- because a salt containing both a large cation and a large anion will dissociate more easily in solution than any other size combination of ions (Marcus, 1985). Greater dissociation will liberate more SCN^- anions to break water structure and reduce viscosity. Although the data presented here are not as definitive for model Kraft lignin solutions, Figure 9 suggests that the trend observed in black liquor is also obeyed in lignin solutions at high salt concentrations and that lignin is one of the principal black-liquor components affected by the added SCN^- salts.

Although the general trend identified for black liquor and lignin in Figure 9 seems to be identical, black-liquor samples exhibit a more pronounced difference in viscosity reduction on cation substitution than is observed with lignin samples. A possible explanation for this discrepancy may lie in the complex composition of black liquor. Chemical components other than lignin, such as polysaccharides or surfactants, may be "salted" into solution along with lignin. These constituents of black liquor are organic macromolecules (Table 1), and, in principle, should also become more water soluble in the presence of a structure-breaking salt. Whereas viscosity reduction due solely to salted-in lignin is measured in lignin solutions, black-liquor viscosity data reflect the collective salting-in behavior of many components simultaneously. Thus, it is not surprising that the magnitude of salt-induced viscosity reduction should differ between lignin and black-liquor solutions.

Conclusions

This work demonstrates that black-liquor viscosity reduction through addition of thiocyanate salts is extremely promising. The salting-in approach described here yields significant viscosity reduction in black liquors at various solids concentrations. The observed increase in viscosity reduction at higher solids content constitutes an extremely useful feature since most processing problems are caused by the high viscosities accompanying high-solids liquor. Results obtained here indicate that the most consistent reduction in viscosity is achieved with neutral thiocyanate salts, although acidic salts will yield the desired effect, provided that the liquor pH remains above ~11.8–12.0. For maximum viscosity reduction, a cation with a large radius should be paired with the SCN^- anion. In this study, GuSCN exhibits the greatest potential as a neutral, viscosity-reducing salt. Black-liquor viscosity can also be tailored by judicious concentration of salt, as well as by operating temperature. Correlation between the data obtained for black-liquor and lignin samples suggests that lignin plays a major role in controlling black-liquor viscosity.

Unlike current black-liquor viscosity reduction approaches, this salting-in method requires minimal capital expenditure for immediate implementation, and it does not involve high-energy input. Such low cost and energy savings can greatly facilitate pulp processing of high-solids black liquor. Control of black-liquor viscosity by salting-in will also prevent environmental pollution, since processing and burning black liquor at high solids contents will reduce SO_2 emissions (Ryham and Nikkanen, 1992; Roberts et al., 1996). In essence, this study lays the foundation for a new approach to controlled black-liquor viscosity reduction and enhanced production of pulp in an energy-efficient and environmentally acceptable manner. In addition, the findings of this study strongly suggest that salting-in, particularly with thiocyanate salts, can be an effective way to tailor the viscosity of aqueous polymer systems.

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Literature Cited

Atkins, P. W., *General Chemistry*, Chaps. 13 and 15, Scientific American Books, New York (1989).

Balzer, D., "Cloud Point Phenomenon in the Phase Behavior of Alkyl Polyglucosides in Water," *Langmuir*, **9**, 3375 (1993).

Boone, M. T., "Recovery Enhancement Through Ultra High Solids," *Tapi Kraft Recovery Operations Short Course*, Tappi Press, Atlanta, p. 93 (1991).

Conway, B. E., *Ionic Hydration in Chemistry and Biophysics*, Chap. 20, Elsevier, Canada (1981).

Edsall, J. T., and J. Wyman, *Biophysical Chemistry*, Vol. 1, Chap. 5, Academic Press, New York (1958).

Ferry, J. D., *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York (1980).

Frank, H. S., and M. W. Evans, "Free Volume and Entropy in Condensed Systems," *J. Chem. Phys.*, **13**, 507 (1945).

Frank, H. S., and W.-Y. Wen, "Ion Solvent Interaction (III)," *Disc. Farad. Soc.*, **24**, 133 (1957).

Frederick, W. J., and T. Adams, "Black Liquor Thermal and Transport Properties," *1992 Kraft Recovery Operations Short Course*, Tappi Press, Atlanta, p. 97 (1992).

Gierer, J., "Chemical Aspects of Kraft Pulping," *Wood Sci. Technol.*, **14**, 241 (1980).

Israelachvili, J., *Intermolecular and Surface Forces*, 2nd ed., Chap. 8, Academic Press, New York (1992).

Lindstrom, T., "The Colloidal Behavior of Kraft Lignin (I)," *Colloid Poly. Sci.*, **257**, 277 (1979).

Luck, W. A., *Water in Polymers*, S. P. Rowland, ed., Chap. 3, ACS Symp. Ser., No. 127 (1980).

MacDonald, R. G., ed., *Pulp and Paper Manufacture*, Vol. 1, 2nd ed., Chaps. 2 and 8, McGraw-Hill, New York (1969).

Malmsten, M., and B. Lindman, "Self-assembly in Aqueous Block Copolymer Solutions," *Macromol.*, **25**, 5440 (1992).

Mandel, M., *Chemistry and Technology of Water Soluble Polymers*, C. A. Finch, ed., Chap. 10, Plenum Press, New York (1983).

Marcus, Y., *Ion Solvation*, Wiley-Interscience, Chichester (1985).

Melander, W., and C. Horvath, "Salt Effects on Hydrophobic Interaction in Precipitation and Chromatography of Proteins," *Arch. Biochem. Biophys.*, **183**, 200 (1977).

Mikhailov, I. G., and Y. P. Syrnikov, "The Influence of Ions in the Structure of Water," *J. Struct. Chem.*, **1**, 10 (1960).

Milanova, E., and G. M. Dorris, "Effects of Residual Alkali Content on the Viscosity of Kraft Black Liquor," *J. Pulp Paper Sci.*, **16**, J94 (1990).

Prevysh, V. A., R. J. Spontak, and S. A. Khan, *Polymers in Medicine*, A. G. Mikos, K. W. Leong, M. L. Radomsky, J. A. Tamada, and M. J. Yazemski, eds., *Mat. Res. Soc. Symp. Proc.*, Pittsburgh, p. 137 (1995).

Prevysh, V. A., B.-C. Wang, S. A. Khan, and R. J. Spontak, "Salting-in of the Aqueous Hydroxypropylcellulose Mesophase through the Addition of Guanidine Thiocyanate," *ACS Poly. Prep.*, **37**(1), 779 (1996a).

Prevysh, V. A., B.-C. Wang, and R. J. Spontak, "Effect of Added Salts on the Stability of Hydrogen-bonded Interpolymer Complexes," *Colloid Poly. Sci.*, in press (1996b).

Prud'homme, R. K., "Rheological Characterization," *Electronic Materials Handbook*, ASM International, Materials Park, OH, p. 838 (1990).

Ramamurthy, P., A. S. Mujumdar, A. R. P. van Heiningen, and G. J. Kubes, "Concentration of Black Liquor to High Solids," *Tappi J.*, **75**, 195 (1992).

Robb, I. D., *Chemistry and Technology of Water-Soluble Polymers*, C. A. Finch, ed., Plenum Press, New York, p. 193 (1983).

Roberts, J. E., R. J. Spontak, H. Jameel, and S. A. Khan, "A Novel Approach to Black Liquor Viscosity Reduction Using Salt Additives," *Tappi J.*, in press (1996).

Ryham, R., "A New Solution to Third Generation Chemical Recovery," *Int. Chem. Recovery Conf.*, Materials Park, OH, p. 581 (1992).

Ryham, R., and S. Nikkanen, "High Solids Firing in Recovery Boilers," *Kraft Recovery Oper. Short Course*, Tappi Press, Atlanta, p. 233 (1992).

Scopes, R. K., *Protein Purification*, 2nd ed., Chap. 3, Springer-Verlag, New York (1987).

Small, J. D., and A. L. Fricke, "Thermal Stability of Kraft Black Liquor Viscosity at Elevated Temperatures," *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 608 (1985).

Smook, J. A., *Handbook for Pulp and Paper Technologists*, 2nd ed., Chaps. 7 and 10, Angus-Wilde, Vancouver (1992).

Soderhjelm, L., "Viscosity of Strong Black Liquor," *Paperi Puu*, **9**, 642 (1986).

Soderhjelm, L., "Factors Affecting the Viscosity of Strong Black Liquor," *Appita*, **41**, 389 (1988).

Soderhjelm, L., "Viscosity of Strong Black Liquor from Sulphate Mills," *Int. Chem. Recovery Conf. Proc.*, Tappi Press, Atlanta, p. 95 (1989).

Spontak, R. J., J. E. Roberts, V. Prevysh, and S. A. Khan, U.S. Patent, filed April 3, 1995.

von Hippel, P. H., and T. Schleich, *Structure and Stability of Biological Macromolecules*, S. N. Timasheff and G. Fasman, eds., Chap. 6, Marcel Dekker, New York (1969a).

von Hippel, P. H., and T. Schleich, "Ion Effects on the Solution Structure of Biological Macromolecules," *Acc. Chem. Res.*, **2**, 257 (1969b).

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