Spectral Monitoring of the Formation and Degradation of Polysulfide Ions in Alkaline Conditions

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The recently developed protocol for the absolute determination of the various polysulfide species based by ^{1}H NMR was applied to monitor the amount of such ions in alkaline media produced at different conditions. The thermal stability of each individual polysulfide species was also evaluated in temperature ranges representative of a typical alkaline pulping process. Overall, the species, S_1^{2-}, S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, and S_6^{2-} were detected and quantified in all alkaline conditions evaluated. The concentration of sodium sulfide and the temperature were found to have a significant effect on the total amount of polysulfides detected. In summary, the di- and trisulfide anions were found to predominate over the other polysulfide species in all examined experimental conditions. Additionally, the experimental values of E_a for the thermal degradation of polysulfide species correlate with the observed stability of the individual species; i.e., S_2^{2-} has the highest E_a, followed by S_3^{2-}.

Introduction

Polysulfide solutions (PS) play an important role in many fields of chemistry, in particular kraft pulping. The benefits from PS addition to the alkaline pulping process have been known for over 50 years.[1] The addition of polysulfide to the white liquor has been shown to oxidize the reducing end groups of polysaccharide chains yielding alkali-stable aldonic acids. This reaction effectively protects both cellulose and hemicellulose from the peeling reactions that are known to take place during pulping.[2,3]

The reactions of PS with lignin and lignin derivatives have also been studied. Jansen and Samuelson[4] showed that dissolved lignin was oxidized by PS present in the cooking liquor during the early stages of cooking. Subsequent efforts by Brunow and Miksche[5] showed that the PS specifically oxidizes enone and quinone methide species during the early stages of pulping. More recently, Berthold and co-workers[6] showed that PS, compared to a standard NaSH cook, increased the rate of degradation of coniferyl alcohol, vinylguaiacol-β-guaiacyl ether, and isoeugenol. Overall, these reports indicate that, in addition to protecting the carbohydrates from the peeling reactions, PS can also oxidize lignin. The delignification rate, however, does not seem to be significantly affected by polysulfide.[7]

Yet, the various efforts aimed at maximizing the pulping yield, via the use of polysulfide, have been carried out in near exclusion of serious fundamental understanding of the underlying chemistry. This is because the precise generation of specific PS species or even the identification of polysulfide species distribution, present in aqueous solution, is exceedingly difficult to obtain.[8,9] The number of sulfur atoms in a polysulfide ion may vary, since the equilibrium governing the formation and degradation of these species is very complex.[10,11] The equilibria between polysulfide ions in aqueous solution can generally be described as follows ($x + y = n + 1$):[12]

$$S_n^{2-} + HS^- + OH^- \leftrightharpoons S_x^{2-} + S_y^{2-} + H_2O \qquad (1)$$
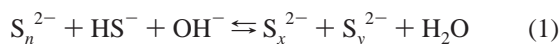
Some variables, such as the chemical environment, temperature, and also the pH, are known to widely affect the

equilibrium. For example, Giggenbach[11,13,14] showed that an equimolar mixture of the tetra- and pentasulfide species is present in aqueous media near neutrality. With increased acidity of the solution, S_2^{2-}, transforms first to S_3^{2-} and S_4^{2-} and finally to S_5^{2-}. In alkaline media, polysulfide anions S_x^{2-} ($x = 2-5$) decompose to thiosulfate along with the net consumption of dissolved sulfur:

$$S_{dissolved} + OH^- \leftrightharpoons {}^1/_4 S_2O_3^{2-} + {}^1/_2 SH^- + {}^1/_4 H_2O \quad (2)$$
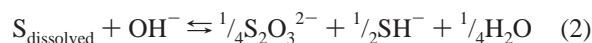
At low alkali concentration, this decomposition reaction causes only a relatively minor loss of polysulfide, while the effect is more pronounced at high polysulfide concentrations.[15] Giggenbach[11] evaluated the equilibrium over the $[H_3O^+]$ range from 0.158×10^{-12} to 3.16×10^{-12} μmol/L at 20 °C and reported that disulfide ions, S_2^{2-}, are the predominant species at extremely high alkalinities, followed by trisulfide ions, S_3^{2-}.

Furthermore, polysulfide solutions are known to be thermodynamically unstable, undergoing oxidation and disproportionation reactions.[15,16] Autooxidation of polysulfides takes place in the presence of oxygen or air, with elemental sulfur and thiosulfate as the products:[16]

$$Na_2S_{2+X} + {}^3/_2 O_2 \rightarrow Na_2S_2O_3 + (x/8)S_8 \qquad (3)$$

Polysulfides can also thermally decompose at higher temperatures to hydrogen sulfide and thiosulfate ions:[10]

$$S_nS^{2-} + (n-1)OH^- + (1-n/4)H_2O \rightarrow$$
$$(1+n/2)HS^- + (n/4)S_2O_3^{2-} \quad (4)$$
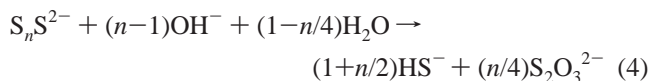
Due to the described intricate reactions involved during the formation and the stability of the various polysulfide species, the actual reactivities of synthetic polysulfide liquors have been determined by monitoring the total amount of polysulfide species. Therefore, a thorough understanding of the precise interaction of specific polysulfides (i.e., S_2, S_3, and S_4, etc.) with the lignocellulosic substrate is essential for the proper design and optimization of polysulfide generating and pulping systems.

Different analytical methods are available for quantifying polysulfide species, such as colorimetric techniques,[17] polaro-

graphic methods,[18] and ion pair chromatography.[19] While most of these approaches are useful in allowing the detection and most likely the quantification of the total amount of species that emerge from the disproportionation of polysulfides, they do not allow the detection and quantification of individual polysulfides species. Individual polysulfide ions can be characterized by their UV absorption properties.[20] The complexity and the need for prior knowledge of the concentration of the original sulfur, sulfides, and alkali-metal hydroxide, however, are obvious disadvantages of such a method. To address the serious limitations of the aforementioned analytical methodologies for detecting and determining the polysulfide species distribution of aqueous polysulfides, we have developed a novel quantitative protocol that allows the absolute determination of the various polysulfide species present in synthetic and industrial pulping liquors.[9] This protocol comprises of alkylating polysulfide ions with dimethyl sulfate followed by quantitative proton NMR spectroscopy using 1,3,5-tri-*tert*-butylbenzene as the internal standard under carefully selected NMR acquisition conditions. In our continuing efforts to better understand polysulfide chemistry, we applied this novel analytical protocol to monitor the effects of the concentration of Na_2S and temperature on the formation of individual polysulfide species. The stability of these species toward thermal degradation in alkaline media was also evaluated.

Materials and Methods

Preparation of Oxygen Free Sodium Hydroxide Solution. Oxygen-free water was prepared by refluxing doubly deionized water for 2 h under a nitrogen atmosphere.[9] A small aliquot of clean mineral oil was finally added to the water to seal it from atmospheric oxygen. The storage flask was always kept under nitrogen, and sampling was carried out using a nitrogen-filled syringe, ensuring that an aliquot below the oil layer was sampled. This solution was used for the preparation of oxygen-free sodium hydroxide solution as follows: Sodium hydroxide (2.88 g, 72 mmol) was weighed in a 20 mL round flask equipped with a three-way stopper and an outlet with a rubber septum. To remove oxygen, a vacuum was first applied and then the flask was filled with argon. Oxygen-free water (12.5 mL) was then added by using a syringe, and the solution was mixed thoroughly until sodium hydroxide was completely dissolved. The resulting solution was kept under argon atmosphere for further use in synthesis of polysulfides.

Synthesis of Inorganic Polysulfides. Sodium sulfide nonahydrate (0.91 g, 3.8 mmol) and elemental sulfur (0.19 g, 6.0 mmol) were measured into a 25-mL round flask equipped with a three-way stopcock. To completely remove oxygen, a vacuum was first applied and then the flask was filled with argon. The reaction mixture was heated (65 °C, 30−40 min) in an oil bath until a homogeneous solution was obtained. Oxygen-free sodium hydroxide (12.5 mL, 5.76 M) was added dropwise into the solution by using a syringe, and the resulting mixture was stirred and heated in the oil bath at temperatures ranging from 40 to 75 °C under argon atmosphere for 2 h. The synthetic polysulfide solutions were allowed to cool to room temperature and used as described in the following sections.

Alkylation and ^1H NMR of Synthetic Polysulfides. Aliquots of 1 mL of the inorganic polysulfides, prepared as described above, were transferred into a 10 mL round-bottom flask. The liquor was stirred, and dimethyl sulfate (1.51 mL) and 0.05 mmol L^{-1} of internal standard (1,3,5-tri-*tert*-butylbenzene in $CDCl_3$) were added dropwise using a syringe over a period of 10 min. After allowing the mixture to react under stirring for 2
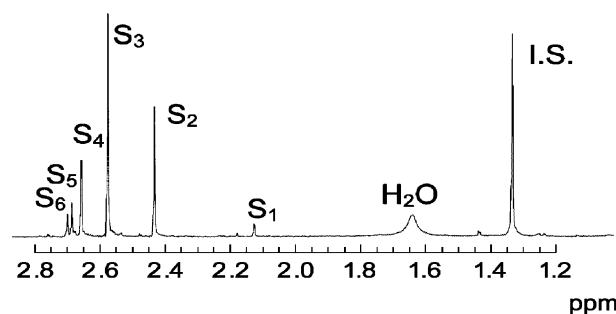

Figure 1. Typical ^1H NMR of synthetic liquor alkylated with dimethyl sulfate in alkaline media. The synthetic liquor was prepared by dissolving elemental sulfur in alkaline Na_2S solution. Peaks: IS = internal standard (1,3,5-tri-*tert*-butylbenzene); $S_1 = (CH_3)_2S_1$; $S_2 = (CH_3)_2S_2$; $S_3 = (CH_3)_2S_3$; $S_4 = (CH_3)_2S_4$; $S_5 = (CH_3)_2S_5$; $S_6 = (CH_3)_2S_6$.

h, the organic phase was separated and a ^1H NMR spectrum was acquired immediately.[9] Spectra were acquired using a Bruker 300 MHz spectrometer equipped with a Quad probe dedicated to ^{31}P, ^{13}C, ^{19}F, and ^1H acquisition. The solvent ($CDCl_3$) peak (δ_H 7.2) was used as an internal reference.

Thermal Degradation of Polysulfides. All thermal degradation experiments were carried out in a metal vessel equipped with a Teflon stopper. About 4 mL of polysulfide solution prepared as described above was transferred into a glass vial, and it was placed inside the metal vessel. After purging with argon to remove any trace of oxygen, the vessel was immediately sealed and immersed in an oil bath set at temperatures ranging from 95 to 170 °C for 2 h. The degraded polysulfide solutions were allowed to cool to room temperature, alkylated, and analyzed by ^1H NMR as described previously.[9]

Results and Discussion

Effect of the Concentration of N_2S and Temperature on the Amount of Individual Polysulfide Species. Figure 1 shows a typical ^1H NMR of synthetic liquor alkylated with dimethyl sulfate under alkaline conditions. Quantification of the different polysulfide species has been done from peak integration using 1,3,5-tri-*tert*-butylbenzene as internal standard. Signal assignments and details of the integration can be found elsewhere.[9,21] The polysulfide species S_1^{2-}, S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, and S_6^{2-} were detected in all synthetic liquors, regardless of the concentration of sodium sulfide or the temperature used in the preparation of the synthetic liquor. When sulfur is refluxed with an alkali solution or soluble sulfide, polysulfide anions are formed.[13] The exact number of polysulfide species existing in an aqueous solution, however, has not been documented with any reproducibility.[8] While some authors believe that the pentasulfide is the longest polysulfide anion in aqueous solution, others state that the hexasulfide is also likely to be present in the aqueous system.[8,22] More recently, Kamyshny et al, using a new methodology based on the determination of methylated polysulfides by liquid chromatography, detected the presence of hepta- and octasulfides in aqueous media.[8] Our data, as we will show, however, are supportive of the presence of hexasulfide as the longest polysulfide species in alkaline media. Longer polysulfide species have not been detected under any conditions examined during this work.

As anticipated, our novel protocol allows for the quantification of individual polysulfide species present in synthetic or industrial liquors.[9] By using this methodology, we examined the effects of different temperatures and concentrations of sodium sulfide on the amount of each individual polysulfide anion under alkaline conditions (Figures 2 and 3). Increasing amounts of
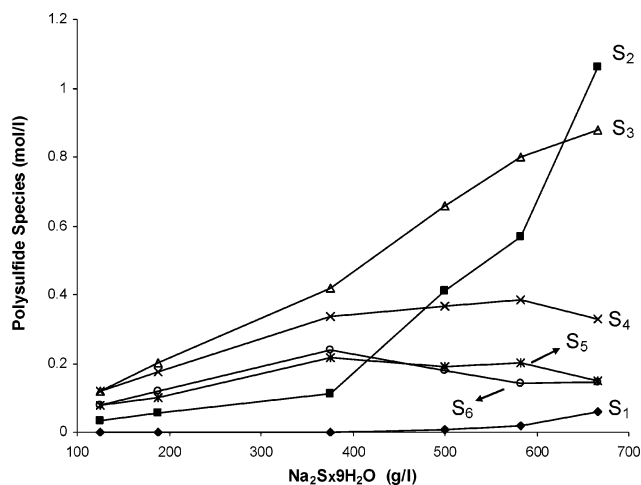
Figure 2. Effect of concentration of $Na_2S \cdot 9H_2O$ on the amount of individual polysulfide species present in an alkaline synthetic liquor. The amounts of polysulfide species are given as moles of each dianion.

sodium sulfide apparently facilitate the formation of most polysulfide anions. As a result, the higher the concentration of sodium sulfide, the higher the amount of polysulfides present in the synthetic liquors (Figure 2). This result indicates that to obtain elevated amounts of polysulfide species, elemental sulfur should be dissolved in liquors containing high sulfidity, instead of high alkalinity. When liquors containing high alkalinity, such as kraft white liquor, are used to dissolve elemental sulfur, excessive amounts of thiosulfate are formed at the expense of polysulfide decomposition.[23] Figure 2 also shows that di- and trisulfide anions predominate over most of the other polysulfide species when higher Na_2S concentrations are used to prepare the synthetic liquor. More specifically, an increase in the concentration of sodium sulfide from 125 to 375 g L^{-1} showed similar effects on the total amount of each individual polysulfide anion (Figure 2). However, higher concentrations of Na_2S have been shown to have a negligible impact on the amounts of tetra-, penta-, and hexasulfide anions, while it increased the amounts of di- and trisulfide species. This is not totally surprising when viewed in the light of the polysulfide rearrangement theory.[24] According to such a theory, the rearrangement reaction rate between OH^-, HS^-, and the different polysulfide ions increases with increased ionic strength. Small polysulfide ions react at a slower rate than larger ions and tend to accumulate in the presence of high ionic strength. Short-chain polysulfide species have also been reported to predominate in increased alkali concentration, with S_3^{2-} becoming dominant in very high alkaline conditions.[11]

The effect of temperature on the amount of individual polysulfide species was evaluated by keeping the concentration of sodium sulfide constant (304 mmol L^{-1}). Our experiments were carried out at temperatures low enough such that thermal decomposition of polysulfides could be considered negligible. In the temperature range evaluated this far (40–75 °C), we observed no significant effect on the content of tetra-, penta-, and hexasulfide anions as evidenced by the data of Figure 3. The amounts of these species were nearly constant up to 75 °C. An increase in the temperature from 40 to 55 °C, however, was found to be beneficial toward the formation of the di- and trisulfide species. Higher temperatures showed negligible effects on the amounts of polysulfide species present in our synthetic liquors.

The di- and trisulfide anions are expected to be the most difficult ones to be formed in aqueous media from the point of view of their Gibbs free energies of formation.[8] In such a way,

the pentasulfide species are believed to be formed preferentially and a mechanism suggesting the rupture of the S_8 ring in sulfur by S^{2-} ion giving rise to pentasulfide ions has been put forward by Haider.[25] Our data, however, pointed out that, in the temperature ranges typical of wood chips impregnation with polysulfide solution, the di- and trisulfide ions are the most dominant polysulfide species. Their high nucleophicity can help explain the beneficial effects of polysulfides on pulp yield by oxidizing the reducing end groups of polysaccharide chains, yielding alkali-stable aldonic acids.[2,3] Additional work is being conducted in our laboratories to evaluate the effect of each individual polysulfide species on the structure of lignin and polysaccharides, which will be the subject of ensuing publications.

Thermal Degradation of individual Polysulfides. One of the main polysulfide consuming reactions during polysulfide pulping is their thermal decomposition.[26] The thermal decomposition of polysulfides in aqueous media starts with a nucleophilic attack of an OH^- ion on a polysulfide ion, followed by formation of sulfide sulfur and thiosulfate. As a rule, the decomposition rate of polysulfide anions is accelerated by increasing temperature, alkalinity, and the ratio of sulfur in oxidation state $S(0)$ versus $S(-2)$. In our efforts, to determine the thermal decomposition of each individual polysulfide ions, we carried out experiments at different temperatures, while maintaining constant the alkalinity and the ratio between polysulfide, excess sulfur, and sulfide sulfur. The range of temperatures evaluated was chosen to be representative of those used in typical pulping processes (95–170 °C).

The degradation reaction rates (k) for each individual polysulfide species were calculated using a first-order reaction (Table 1), and the activation energies for their decomposition were calculated based on a typical Arrhenius plot (Figure 4). The activation energy varied between 45.9 and 13.0 kJ mol^{-1} (Table 2), and it was found to be dependent on the size of the polysulfide ion. In general, the smaller the polysulfide ion, the higher the activation energy for its thermal decomposition. The values obtained for the activation energies are in accordance with those reported by Gustafsson and Teder[24] and point out that the species S_2^{2-} and S_3^{2-} are among the most stable in alkaline media. The S_6^{2-}, however, can be considered as the most unstable species present in the examined systems.

Overall, the degradation rates of all polysulfide anions were found to be strongly affected by temperature (Table 1). As anticipated, the higher the temperature, the faster the degradation reaction. For example, at 145 °C the degradation reaction rate constant of the disulfide was 5.42×10^2 s^{-1}, and it increased 3.4-fold, reaching about 18.6×10^2 s^{-1} at 170 °C. It is worth mentioning here that, in a typical alkaline pulping process, the temperature is ramped from 40 °C to the maximum of 170 °C. Our results indicated that di- and trisulfide would be the most active polysulfide species during alkaline polysulfide pulping. The beneficial activities of polysulfide species, however, will be exerted during the wood chip impregnation stages, when the thermal degradation rate of the different polysulfide species is somewhat lower than in typical pulping conditions. It is likely that as soon as the process reaches its higher operational temperature levels the thermal degradation rate of the polysulfides increases to such a degree where most polysulfide ions are expected to be transformed into thiosulfate and hydrogen sulfide ions.[16]

Conclusions

It was demonstrated that the polysulfide species S_1^{2-}, S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, and S_6^{2-} are present in alkaline media,
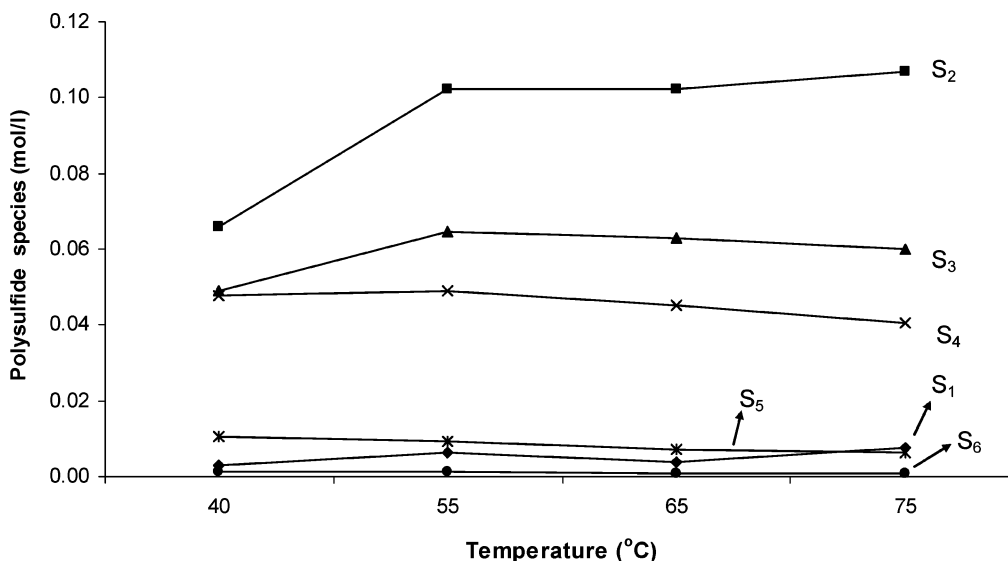
Figure 3. Effect of temperature on the amount of individual polysulfide species present in an alkaline synthetic liquor. The amounts of polysulfide species are given as moles of each dianion.

Table 1. Thermal Degradation Rate Constants (k) for Individual Polysulfide Anions[a]

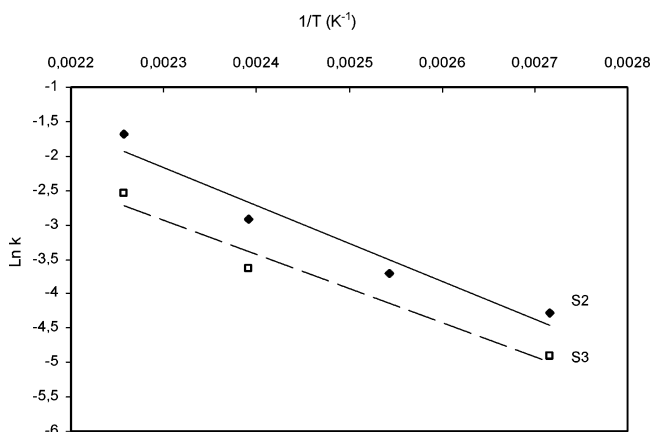| temp (°C)	degradation rate constant $\times 10^2$ (s^{-1})				
	S_2^{2-}	S_3^{2-}	S_4^{2-}	S_5^{2-}	S_6^{2-}
95	1.39	0.73	1.48	1.21	3.26
120	2.46	nd	nd	nd	nd
145	5.42	2.64	2.54	2.42	3.40
170	18.59	7.93	5.77	6.69	7.73

[a] nd = not determined.

Figure 4. Effect of temperature on the degradation of di- and tripolysulfide anions. The data were collected at four different temperatures: 95, 120, 145, and 170 °C.

Table 2. Energy of Activation ($E_{act.}$) for the Degradation of Individual Polysulfides Species in Alkaline Media

polysulfide anion	$E_{act.}$ (KJ mol^{-1})	r^2 (for Arrhenius plot)
S_2^{2-}	45.9	0.95
S_3^{2-}	41.2	0.88
S_4^{2-}	22.7	0.88
S_5^{2-}	28.5	0.89
S_6^{2-}	13.0	0.57

regardless of the temperature and concentration of Na$_2$S. However, S_2^{2-} and S_3^{2-}, seem to predominate at higher Na$_2$S concentrations in higher alkalinities. During polysulfide formation, an increase in the temperature from 40 to 55 °C has been shown to be beneficial toward the formation of di- and trisulfide species. The reaction rate of polysulfide degradation was found to dramatically increase with increasing temperature with S_2^{2-}

and S_3^{2-} being the most stable, i.e., of the highest energy of activation for thermal degradation. In general, the values for the energy of activation for thermal degradation were found to diminish with increased sulfur chain length in good agreement with observed stabilities of individual polysulfide species.

Acknowledgment

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