Thermal and Alkali Stability of Sodium Dithionite Studied Using ATR-FTIR Spectroscopy

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Sodium dithionite ($Na_2S_2O_4$) may have the potential to be used as a reducing agent for the stabilization of glucomannan in kraft cooking for increased pulp yield. However, due to the fact that dithionite decomposes under the conditions of kraft pulping, studies of the effects of dithionite in kraft pulping are non-conclusive; sometimes clearly showing an increased yield, and in other studies no effect at all. The specific conditions influencing dithionite degradation are also unclear. For that reason, this study was conducted to determine the thermal and chemical stability of sodium dithionite with respect to specific factors, such as the pH, temperature, heating time, and the concentration of sodium dithionite solution. The study was performed under anaerobic conditions using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The thermal and alkali stability of the sodium dithionite solution was shown to decrease with increasing temperature, heating time, and concentration of the solution at the alkaline conditions studied. The thermal stability decreased rapidly at weak alkalinity (pH 9) as well as in high alkalinity (pH 14), whereas the sodium dithionite was rather stable at moderate alkalinity (pH 11.5 to pH 13).

Keywords: Alkalinity; Concentration; Dithionite; ATR-FTIR; Stability; Temperature

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INTRODUCTION

The chemical kraft pulp production is a large-scale mill operation in which a key issue for profitability is the yield achieved at a given kappa number, *i.e.*, lignin content. During kraft pulping the glucomannan degradation, caused by the peeling reactions, leads to extensive yield losses early in the cook. For a long time, anthraquinone has been used as a pulping additive, improving the stability of the glucomannan and thus increasing the yield. However, today many mills have abandoned the use of anthraquinone due to questions related to health issues. Thus, alternative additives are being sought in an effort to stabilize the glucomannan. One such strong reducing agent is sodium dithionite ($Na_2S_2O_4$), which has been in use in the pulp and paper industry mainly for its bleaching purposes. In 1952 a study was published indicating an increased yield when dithionite was added to the cooking liquor (Jayme and Wörner 1952a,b). Subsequently, trials have been reported using dithionite in soda and kraft pulping showing non-conclusive results with respect to yield increases (Nilsson and Östberg 1968; Irvine *et al.* 1987; Wang 2014). To some extent, the problem could be related to the fact that dithionite is highly unstable and easily undergoes decomposition, especially at high temperatures or in aerobic conditions (Wayman and Lem 1970). The decomposition of sodium dithionite in solutions has been extensively studied (Lister and Garvie 1959; Burlamacchi *et al.* 1969;

Wayman and Lem 1970; Janzen 1972; Kilroy 1980), but still, the situation with regard to kraft pulping conditions remains unclear.

In pulping the largest part of the glucomannan losses occurs by peeling reactions in the initial phase of impregnation and subsequent heating to the cooking temperature (Sjöström 1977). Using a reductive stabilisation, as of dithionite, a stable end molecule of the glucose unit, an alcohol, is achieved (Aurell and Hartler 1963). Thus, it would be sufficient in reducing the losses of glucomannan if stabilisation could be accomplished under the initial pulping conditions. This could involve temperatures not reaching above 120 °C.

The generally accepted decomposition reaction of sodium dithionite in a water solution under anaerobic conditions is to form sodium bisulphite ($NaHSO_3$) and sodium thiosulphate ($Na_2S_2O_3$) (Burlamacchi *et al.* 1969):

$$2\ Na_2S_2O_4 + H_2O \rightarrow 2\ NaHSO_3 + Na_2S_2O_3 \qquad (1)$$

In a weak alkaline medium, sodium thiosulphate, sodium sulphite (Na_2SO_3), and water are formed according the following reaction (Lister and Garvie 1959):

$$2\ Na_2S_2O_4 + 2\ NaOH \rightarrow Na_2S_2O_3 + 2\ Na_2SO_3 + H_2O \qquad (2)$$

In a strong alkaline medium the following reaction occurs, where sodium sulphite, sodium sulphide (Na_2S), and water are formed (Greenwood and Earnshaw 1984),

$$3\ Na_2S_2O_4 + 6\ NaOH \rightarrow 5\ Na_2SO_3 + Na_2S + 3\ H_2O \qquad (3)$$

The decomposition of sodium dithionite is mainly affected by the concentration of dithionite and the pH of the solution (Rinker *et al.* 1960). The dithionite ion ($S_2O_4^{2-}$) decomposes rapidly in acidic conditions or at high temperatures (even under anaerobic conditions). The decomposition of the dithionite ion is accelerated by increasing acidity, a higher concentration of the dithionite ion, increased temperature, and other sulphur-containing species (Wayman and Lem 1970; Kilroy 1980). Under alkaline conditions the decomposition of sodium dithionite has been shown to be slower (Greenwood and Earnshaw 1984), but detailed information regarding the role of the pH with varying temperature, time, and concentration of the solution has not yet been fully determined.

The decomposition of sodium dithionite can be determined by different methods, such as: iodometry, potentiometry, spectrometry titrations, ion chromatography, and electroanalytical methods (Fox 1974). Due to the instability of sodium dithionite with oxygen, the decomposition of sodium dithionite should be evaluated under strictly anaerobic conditions. Sulphur-oxygen (S-O) compounds have relatively intense stretching modes, and these are readily observed in the low wavenumber region of the infrared spectrum (*i.e.*, 1350 cm^{-1} to 750 cm^{-1}) (Holman *et al.* 1994). In attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, the radiation interacts with the sample mainly at the sample interface, resulting in a very short and effective path length. This makes ATR-FTIR spectroscopy an ideal candidate for the research of sodium dithionite decomposition reactions. In this study, the decomposition of sodium dithionite at conditions relevant for kraft pulping was examined using ATR-FTIR spectroscopy. The effects of three different temperatures (80 °C, 100 °C, and 120 °C), of varying alkaline conditions (pH 9, pH 11.5, pH 12.5, pH 13, and pH 14), of time (10 min, 20 min, 30 min, 40 min, and 60 min), and of different concentrations (*i.e.*, molarities; mol/L) of sodium dithionite (0.2 M, 0.4 M, and 0.6 M) were evaluated.

EXPERIMENTAL

Materials

The chemicals used in this study were sodium dithionite ($Na_2S_2O_4$) (≥ 85% purity), sodium hydroxide (NaOH), sodium thiosulphate ($Na_2S_2O_3$), and sodium sulphite (Na_2SO_3); Merck KGaA (Darmstadt, Germany) supplied all of these chemicals.

Sample preparation

Sodium dithionite solutions were prepared under anaerobic conditions in a Plexiglas box continuously purged with nitrogen gas. Three different concentrations (*i.e.*, 0.2 M, 0.4 M, and 0.6 M) of the dithionite solutions were prepared in 50-mL volumetric flasks (previously purged with nitrogen) by mixing the required amounts of sodium dithionite with deionized water (purged with nitrogen). The pH of these solutions was then adjusted. For the solution having a pH of 9, deionized water, only, was used for the preparation. For the solutions having a pH of 11.5, pH of 12.5, pH of 13, and pH of 14, the desired pH was adjusted by adding the required amount of sodium hydroxide. Aliquots of 10 mL were taken from each solution and kept at 20 °C; these were labelled as the reference solutions having a defined pH and concentration. The rest of the prepared solutions, as described earlier, were then transferred to preheated Teflon autoclaves with stainless steel caps (also previously purged with nitrogen), 10 mL in volume, and placed in a preheated oil bath (at temperatures of 80 °C, 100 °C, or 120 °C) for the specified times for decomposition. These solutions were labelled as the sample solutions. After completing the heating period, the autoclaves were placed in a water bath adjusted to 10 °C for 40 min for cooling.

All of the solutions were continuously measured, directly after the preparation. For the dithionite concentration of 0.4 M three replicates were measured at all conditions. For the dithionite concentration of 0.2 M and 0.6 M single measurements were performed. In addition, a pure sodium dithionite solution having a pH of 8 was also prepared, and then kept at 20 °C for recording a spectrum of undecomposed sodium dithionite.

Methods

ATR-FTIR spectroscopy

The ATR-FTIR spectra of the reference and sample solutions were recorded using a Varian 680-IR FTIR spectrometer (Varian Inc., Santa Clara, CA, USA), equipped with a Pike MIRacle ATR crystal consisting of a single reflection diamond with a w/ZnSe crystal plate (Pike Technologies Inc., Madison, WI, USA). The ATR crystal had a contact area of 2-mm in diameter (Ø). The penetration depth of the infrared (IR) radiation was 2 µm. The ATR crystal was constantly purged with nitrogen by placing a specially designed hood over the crystal. For each reference solution (20 °C) and for each sample solution (10 °C), 2 drops were placed on the ATR-FTIR crystal (directly after the preparation) and a spectrum was recorded under a nitrogen atmosphere. The spectra were stable under these conditions. The background spectra and sodium dithionite spectra were scanned and collected with a spectral resolution of 4 cm^{-1} in a spectral range of 4000 cm^{-1} to 525 cm^{-1}; 24 scans were collected. The average spectra were calculated and the baseline was corrected at the wavenumbers of 3800 cm^{-1}, 1880 cm^{-1}, and 1300 cm^{-1}. The software used was Varian Resolutions Pro (Varian Inc., Santa Clara, CA, USA) (Version 5.1).

Spectral evaluations

The thermal/alkali stability of the sodium dithionite solutions was evaluated from the height of the dithionite ion ($S_2O_4^{2-}$) signal (*i.e.*, the SO_2 group asymmetric stretching), appearing at 1051 cm^{-1} in the infrared spectrum. The thermal/alkali stability was expressed as the relative percentage (%) of dithionite remaining in the solution and was calculated according to Eq. 4,

$$\text{Relative } \% \ remaining = \left(\frac{I_0 - I}{I_0}\right) \cdot 100 \tag{4}$$

where I_0 is the height (a.u., *i.e.*, absorbance units) of the dithionite ion signal of the reference solution and I is the height (a.u.) of the dithionite ion signal of the corresponding sample solution. For each solution measured, the height of the signal of the dithionite ion was evaluated by drawing a new baseline at the base of the 1051 cm^{-1} signal between two minimal points, as illustrated in Fig. 1.

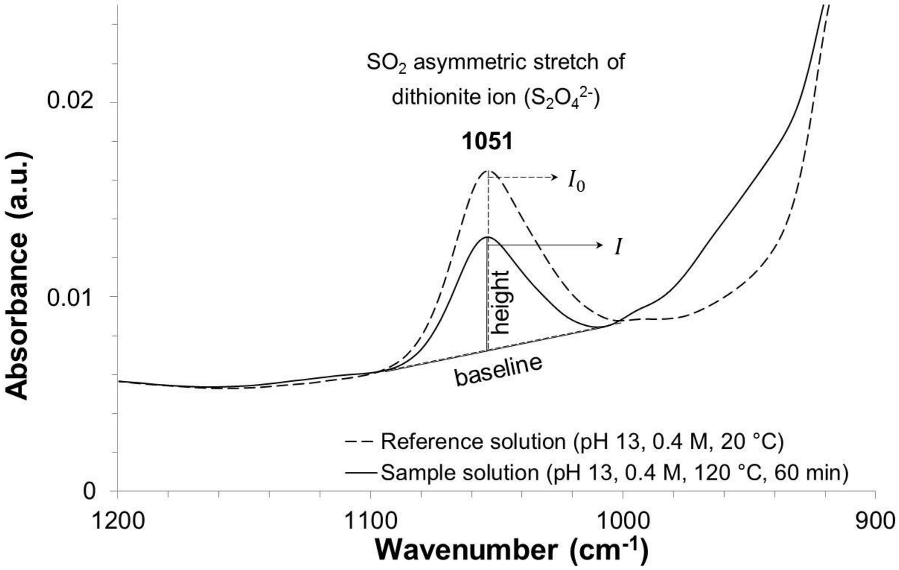

Fig. 1. ATR-FTIR spectra in the wavenumber region from 1200 cm^{-1} to 900 cm^{-1} of a 0.4 M reference solution of sodium dithionite having a pH of 13 at 20 °C (dashed line) and of a 0.4 M corresponding sample solution of dithionite solution having a pH of 13 after heating at 120 °C for 60 min (solid line). The figure illustrates the procedure for evaluating the thermal/alkali stability of dithionite, where I_0 is the height of the dithionite ion signal of a reference solution and I represents the height of the dithionite ion signal of a sample solution.

Multivariate analysis

A multivariate data analysis of the ATR-FTIR spectra was performed using SIMCA-14 (Umetrics AB, Umeå, Sweden) (Version 1998-2015). A principle component analysis (PCA) was performed where the PCA is a projection method that describes the systematic variation in a data table X with a few latent variables called scores, T.

RESULTS AND DISCUSSION

Spectral Analysis

To determine the factors of importance regarding the thermal and alkali stability of dithionite, the measurements were performed as a function of concentration (0.2 M, 0.4 M, and 0.6 M), of pH (pH 9, pH 11.5, pH 12.5, pH 13, and pH 14), and of temperature (80 °C, 100 °C, and 120 °C) at different heating times (10 min, 20 min, 30 min, 40 min, and 60 min). The effect of the different parameters (pH, temperature, and heating time) on the thermal and alkali stability was first evaluated using a multivariate analysis on the sodium dithionite solutions having the concentration of 0.4 M (Fig. 2). The spectra, *i.e.* nine spectra per pH value, in the wavenumber region of 1200 cm^{-1} to 800 cm^{-1} were utilized. As seen from the score scatter plot of the two first components, *t1* and *t2*, three groups were distinguished: (a) one group in the lower pH range (pH 9 and pH 11.5), and (b) one group at the higher pH range (pH 14), in which those particular solutions were unstable, and (c) one group in the middle pH range (pH 11.5 to pH 13), and those particular solutions were rather stable. Overlaps were noticed for the group with a pH of 11.5, where all of the solutions at 80 °C and one solution at 100 °C (20 min), presented with yellow circles in group (c), were rather stable. For the group with a pH of 12.5, only one outlier was seen, *i.e.*, the solution at 120 °C and 60 min, presented with dark blue square in group (a), which appeared as unstable (*cf.* Figs. 5 through 7). The first component, *t1,* reflects base-line shifts together with a low absorption from dithionite. The second component, *t2,* reflects the degradation of dithionite to thiosulphate (wavenumbers 1055 cm^{-1} and 921 cm^{-1} positive, 1110 cm^{-1} and 995 cm^{-1} negative).

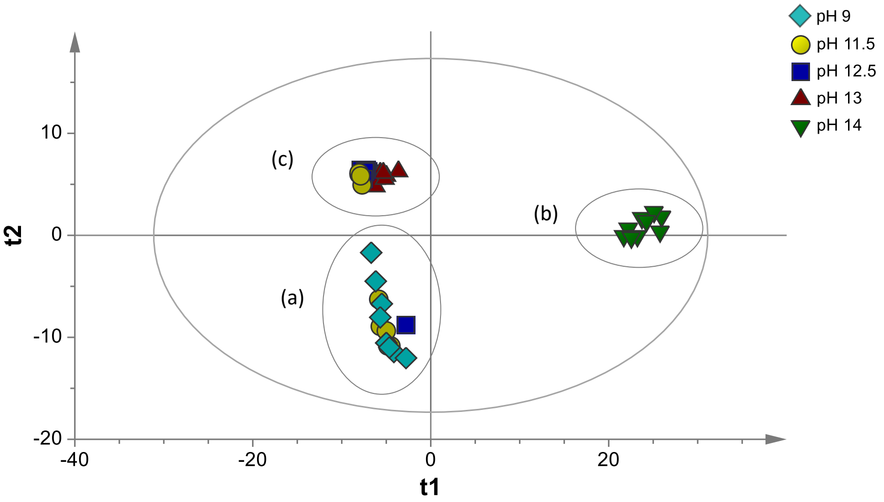

Fig. 2. Score scatter plot, *t1 vs. t2*, of the ATR-FTIR spectra in the wavenumber range from 1200 cm^{-1} to 800 cm^{-1} for the dithionite solutions having the concentration of 0.4 M

The different behaviour of these three groups was clearly apparent in the ATR-FTIR spectra taken at the different pHs (Fig. 3). For the prepared solutions of pure sodium dithionite (pH 8), two signals could be seen, at 1051 cm^{-1} and 912 cm^{-1}, as characteristic vibrations for the SO_2 asymmetric and the SO_2 symmetric stretch of the dithionite ion ($S_2O_4^{2-}$), respectively (Takahashi *et al.* 1982). For the decomposed solutions with a pH of 9, pH of 11.5, and a pH of 12.5, the signal was seen at 995 cm^{-1}, which indicated the presence of thiosulphate ions ($S_2O_3^{2-}$) (Strassburger and Breuer 1985; Holmen *et al.* 1994). The simultaneously occurring small signals, observed at 1108 cm^{-1} and 1022 cm^{-1}, were assigned to the S=O asymmetric stretch and the S=O symmetric stretch of thiosulphate, while the signal at 995 cm^{-1} was assigned to the SO_2 symmetric stretching for the thiosulphate ion. For the solution with a pH of 13, the two dithionite ion signals (at 1051 cm^{-1} and 912 cm^{-1}) were seen as for the pure sodium dithionite solution (pH 8). The two signals for the sodium dithionite solution at pH 13 were lower in intensity than the corresponding signals for the pure sodium dithionite solution (pH 8). Also, a third signal, which appeared as a shoulder, was visible in the region for absorbance of the sulphite ion (SO_3^{2-}). Similar behaviour was also seen in the spectra for the solution with a pH of 12.5 (*i.e.*, the signal at 912 cm^{-1} and shoulder at 925 cm^{-1} appeared as somewhat lower in intensity). For the decomposed solution (pH 14) only a strong and broad signal appeared at 925 cm^{-1}, which indicated the presence of sulphite ions (Takahashi *et al.* 1982). The signal at 925 cm^{-1} was assigned to the S-O stretch of the sulphite ion.

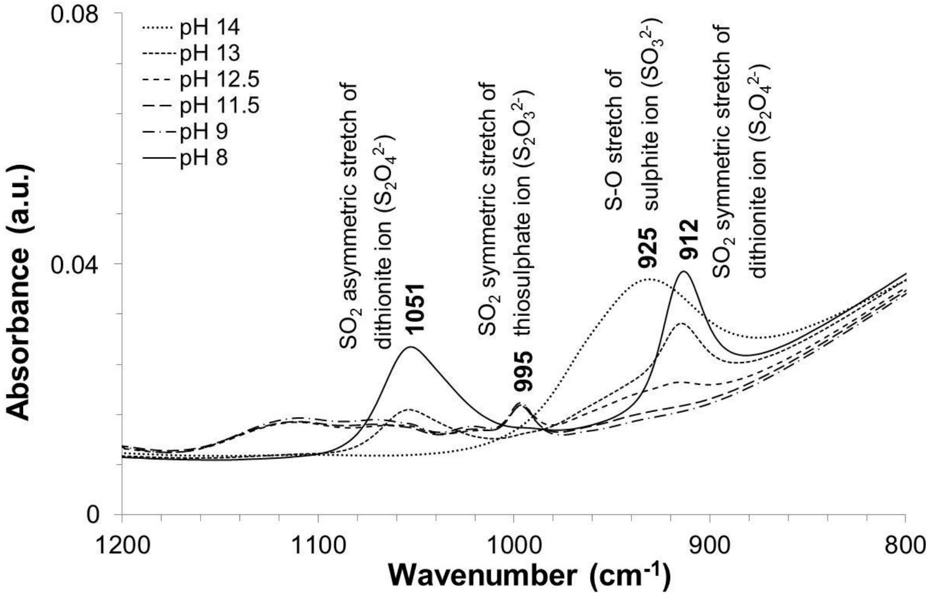

Fig. 3. ATR-FTIR spectra in the wavenumber range from 1200 cm^{-1} to 800 cm^{-1} for the 0.4 M dithionite solutions having different pHs, subjected to 120 °C for 60 min; for comparison a spectrum of an undecomposed solution of pH 8 taken at 20 °C is included (solid line)

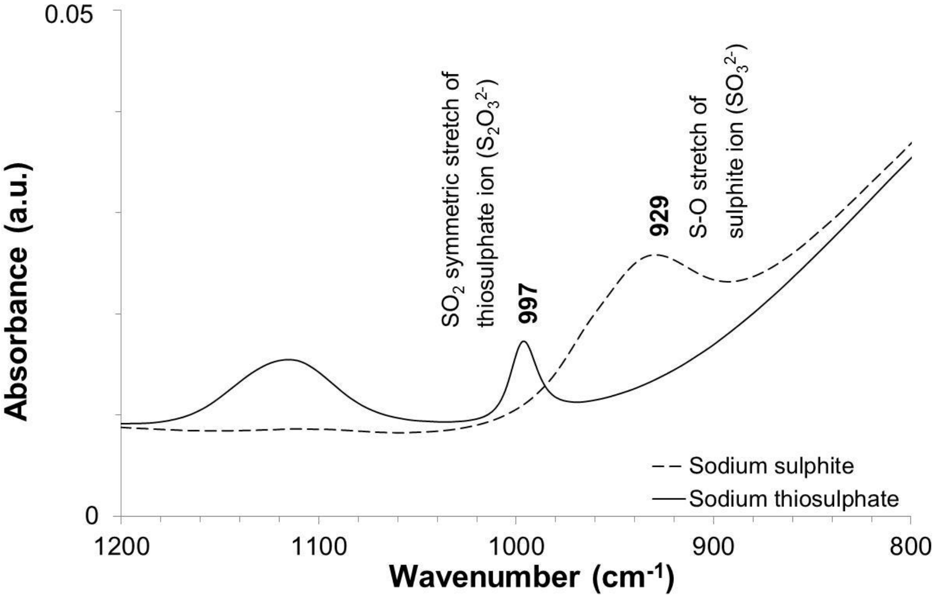

Fig. 4. ATR-FTIR spectra in the wavenumber range from 1200 cm^{-1} to 800 cm^{-1} for the sodium sulphite (dashed line) and sodium thiosulphate (solid line) solutions

For comparison, an ATR-FTIR spectrum was taken of the pure components of thiosulphate and sulphite, respectively (Fig. 4), where the thiosulphate ions ($S_2O_3^{2-}$) absorbed at 997 cm^{-1} and the sulphite ions (SO_3^{2-}) absorbed at 929 cm^{-1}. These spectra thus confirmed the assignments made for the decomposed solutions.

Effect of pH and Temperature

To evaluate the importance of the different factors involved in the dithionite decomposition, solutions of the molarity of 0.4 M were chosen for a more extensive study. For each condition, three replicates were performed. Figures 5 through 7 show the effects of the pH on the relative stability of the sodium dithionite solutions for different heating times at the different temperatures of 80 °C, 100 °C, and 120 °C, respectively.

From Figs. 5 through 7, it was obvious that the stability of the sodium dithionite solutions decreased as the heating time increased, more so at the higher (pH > 13) and lower (pH < 12.5) pHs. It was also clear that with increasing temperature the rate of decomposition increased. In fact, at 120 °C, the decomposition was so rapid at pHs below 12.5 that all of the dithionite had decomposed already at 20 min. For the samples fully decomposed, the pH had decreased by some tenths of a unit. In contrast, at pHs of 12.5 and 13, the sodium dithionite was fairly stable even at a temperature of 120 °C.

Reaction rate

A further analysis of the temperature dependence of the reactions was made by estimating the activation energy E_a for the reactions at a pH of 9 and pH of 14, respectively, utilizing the Arrhenius equation, as expressed by Eq. 5,

$$k = A \cdot e^{-\left(\frac{E_a}{RT}\right)} \tag{5}$$

where k is the reaction rate of the coefficient (*e.g.*, s^{-1}, if a first-order reaction), A is the frequency factor for the reaction (s^{-1}, if a first-order reaction), E_a is the activation energy

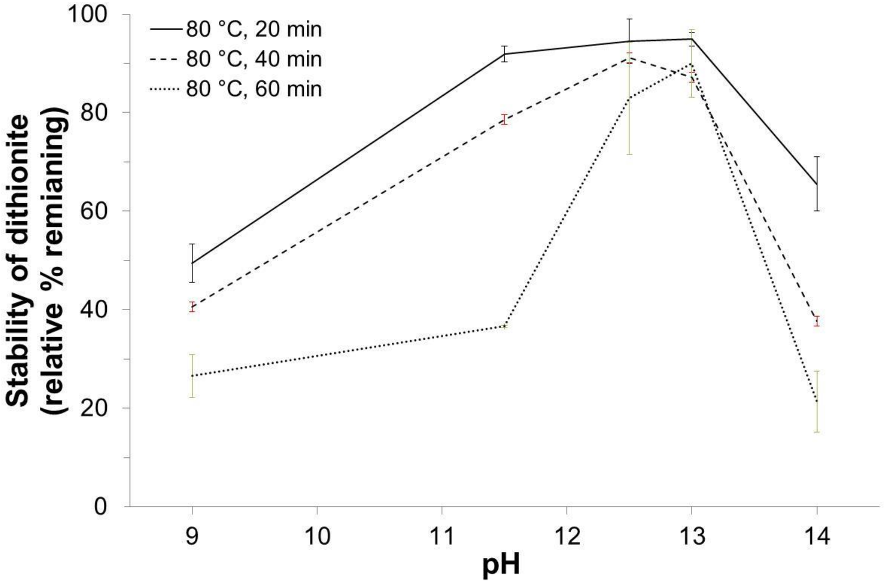

Fig. 5. Stability of 0.4 M sodium dithionite solutions as a function of pH at a temperature of 80 °C for heating times of 20 min, 40 min, and 60 min. Standard deviation of three replicates is indicated by bars (black for 20 min, red for 40 min and green for 60 min heating time).

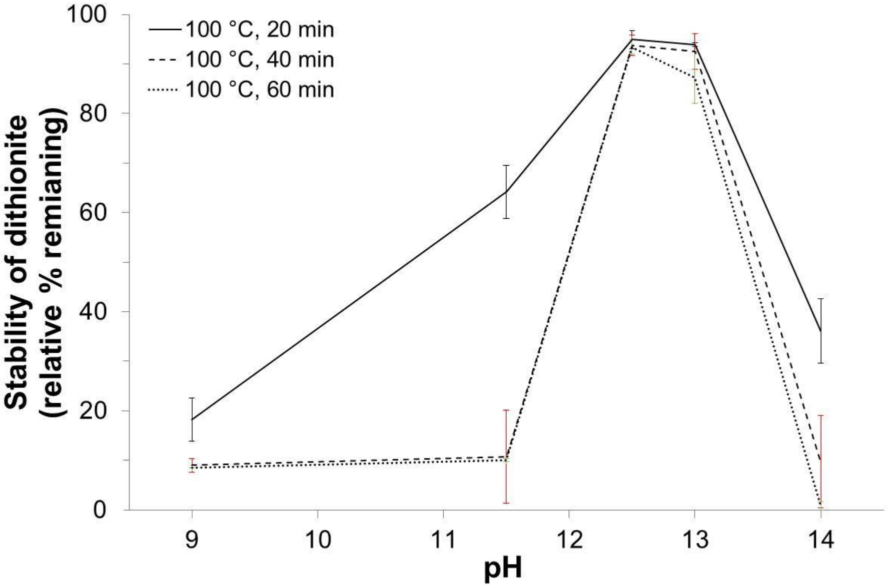

Fig. 6. Stability of 0.4 M sodium dithionite solutions as a function of pH at a temperature of 100 °C for heating times of 20 min, 40 min, and 60 min. Standard deviation of three replicates is indicated by bars (black for 20 min, red for 40 min and green for 60 min heating time).

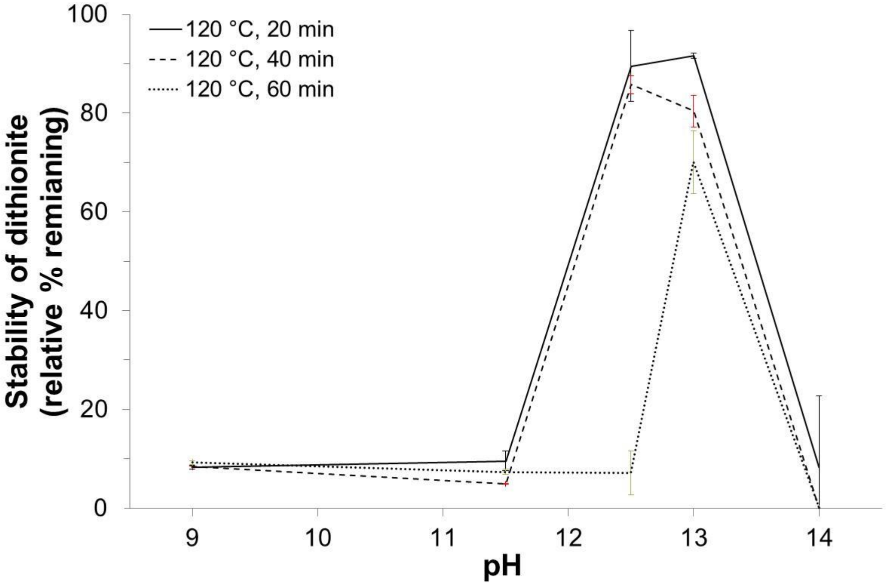

Fig. 7. Stability of 0.4 M sodium dithionite solutions as a function of pH at a temperature of 120 °C for heating times of 20 min, 40 min, and 60 min. Standard deviation of three replicates is indicated by bars (black for 20 min, red for 40 min and green for 60 min heating time).

(kJ/mol), R is the universal gas constant (= 8.315 J/mol·K), and T is the temperature (K). As the rate coefficient is a function of time (*i.e.*, $1/t$), ln ($1/t$) is plotted *versus* $1/T$ in an Arrhenius diagram for the two reaction types, respectively (Fig. 8, (a) pH 9 and (b) pH 14). The rate of degradation was taken at 50% of the dithionite decomposition. It was obvious that at a pH of 9 the concentration of dithionite had no influence on the rate of degradation, whereas for the pH of 14, the higher the concentration of dithionite was, the faster was the decomposition. From the slopes an apparent activation energy (E_a) for the reactions at pH of 9 and pH of 14 could be calculated by 40 kJ/mol ± 5 kJ/mol and 55 kJ/mol ± 10 kJ/mol, respectively. These values could be compared to the activation energy of 110 kJ/mol estimated for the dithionite decomposition (for a supposedly first order reaction studied in the temperature interval of 80 °C to 100 °C) at pH of 13 (Lister and Garvie 1959).

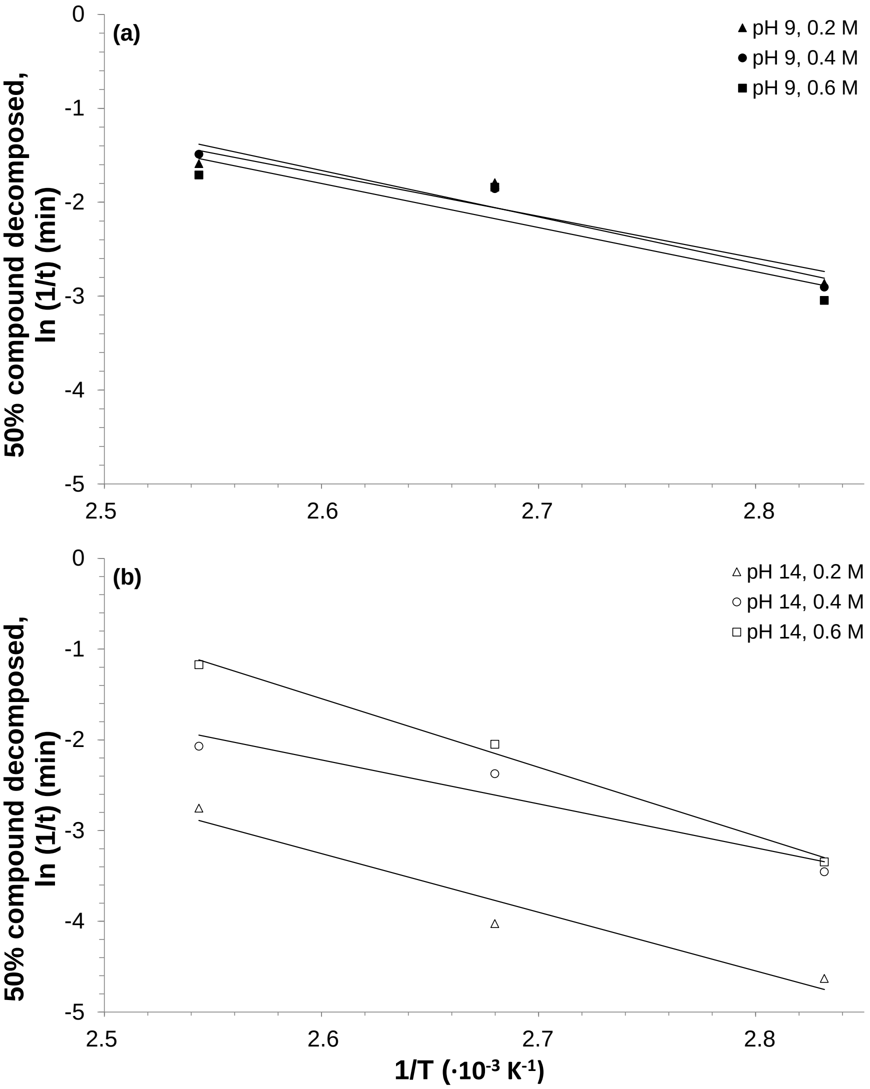

Fig. 8. Arrhenius plot of the reaction time, *i.e.*, ln (1/*t*) as a function of *1/T* for sodium dithionite solutions of 0.2 M, 0.4 M, and 0.6 M at (a) pH of 9 and (b) pH of 14

Relation to pulping

The studies here performed regarding the alkali stability of sodium dithionite under anaerobic conditions clearly pointed out that a window existed in the pH interval between pH 12.5 to pH 13 where dithionite was considerably more stable than at lower and higher pHs. With increasing temperature, the rate of decomposition increased, in the studied temperature interval 80 °C to 120 °C, but even at 120 °C dithionite was rather stable at a pH of 13.

In kraft pulping, the impregnation liquor usually has a pH close to 14, which makes the use of dithionite impossible. However, in the impregnation phase of the cooking, a large amount of alkali would have been consumed in the neutralising of the acids of the wood polymers. If first a neutralisation could take place without too severely degrading glucomannan, a second impregnation with dithionite for stabilising the glucomannan could be feasible. Such a scheme would rely on the possibility of maintaining the solution in the pH interval of more stable dithionite conditions. These matters have to be further researched.

At a lower pH, the decomposition rate seemed to be rather independent of the dithionite concertation, whereas at the higher pH, *i.e.*, pH of 14, the decomposition increased with the concentration. This was in line with the results of Lister and Garvie (1959), who found that the rate of decomposition increased somewhat at higher sodium dithionite concentrations.

CONCLUSIONS

1. The stability of an alkaline (excluding the pH range of 12.5 to 13.0) sodium dithionite solution, under anaerobic conditions, decreased with increasing temperature, heating time, and to some extent the concentration of the solution.
2. The stability decreased rapidly at weak (pH 9) and strong (pH 14) alkaline conditions according to two different mechanisms. At moderate pHs (pH 11.5 to 13) the sodium dithionite solution appeared to be rather stable.
3. At the different pH ranges, two different decomposition products were formed, *i.e.*, thiosulphate ($S_2O_3^{2-}$) at pHs of 9 to 12.5, and sulphite (SO_3^{2-}) at a pH of 14.
4. The possibility of using alkaline dithionite solutions of pHs around pH 13 for stabilising glucomannan for kraft pulping could be worth further researching.

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