Quantitative ¹H NMR analysis of alkaline polysulfide solutions

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Abstract

A novel analytical protocol for the absolute determination of the various polysulfide species present in alkaline aqueous media was developed. The method is comprised of alkylating polysulfide ions with dimethyl sulfate, followed by quantitative proton NMR spectroscopy using 1,3,5-tributyl benzene as the internal standard. In order to arrive at a quantitative acquisition protocol, a number of variables were examined in detail for their effect on the alkylation reaction, including the presence of oxygen, the amount of dimethyl sulfate and sodium hydroxide, and the various modes of adding the alkylating reagent to the reaction mixture. Most of these variables were found to play a role in determining the quantitative reliability of the procedure. Consequently, a method is described that can be used for the efficient and reliable quantitative detection of polysulfide ions. The protocol developed could be particularly useful in promoting our understanding of the intricate and delicate chemistry of polysulfide equilibria in aqueous alkaline media.

Keywords: alkylation; dimethyl sulfate; nuclear magnetic resonance (NMR); polysulfide; pulping liquor.

Introduction

The pulp and paper industry uses polysulfide solutions in green and white liquors, in which their beneficial effects on pulp yield, viscosity, and degree of lignin removal have been demonstrated (Li et al. 1998; Munro et al. 2001). In gold mining, polysulfides are used as leaching agents to replace the environmentally problematic cyanides (Moore 1986), while polysulfide solutions also find significant utilization in solar, photoelectrochemical and conventional cell production (Steudel et al. 1986; Licht 1989).

Polysulfide solutions are thermodynamically unstable, since they can readily undergo oxidation and disproportionation reactions. Autooxidation of polysulfides takes place in the presence of oxygen, with elemental sulfur and thiosulfate as the only products:

$$Na_2S_{2+x} + 3/2O_2 \rightarrow Na_2S_2O_3 + x/8S_8 \qquad (1)$$
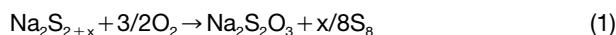
In alkaline media, polysulfide anions S_x^{2-} (x = 2–5) decompose to thiosulfate along with the net consumption of dissolved sulfur (Licht and Davis 1997):

$$S_{dissolved} + OH^- \rightleftharpoons 1/4S_2O_3^{2-} + 1/2SH^- + 1/4H_2O \qquad (2)$$
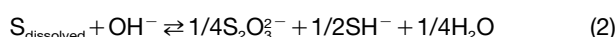
However, if the polysulfide concentration is high (>5 mol L^{-1}) and the alkali concentration relatively low (<2 mol L^{-1}), then this reaction causes only a relatively minor loss of polysulfide ions (Licht and Davis 1997). Under such conditions the half-life of zero-valent sulfur is of the order of years. Giggenbach (1974) also arrived at similar conclusions to those of Steudel et al. (1986), who reported that in near-neutral sulfide solutions, polysulfide ions resist disproportionation at up to 240 °C, while at pH values greater than 8, polysulfide ions become metastable, even at room temperature.

The number of sulfur atoms in a polysulfide ion may vary according to Eq. (3) (Giggenbach 1972). In a polysulfide solution made from $Na_2S \cdot 9H_2O$, NaOH, Na_2S_4 and a borate buffer, the distribution of S_nS^{2-} (n = 1–4) and HS^- is known to be strongly influenced by the pH of the solution. With increased acidity of the solution, the predominant species, S_2^{2-}, switches first to S_3^{2-} and S_4^{2-}, and then to S_5^{2-}. The latter was found under nearly neutral or slightly acidic conditions.

$$nS_mS^{2-} + SH^- + OH^- \rightleftharpoons mS_nS^{2-} + H_2O \qquad (3)$$

The dissociation energy of the S–S bond in polysulfide (138–151 kJ mol^{-1}) is much lower than that of the S–S bond in disulfide (272–293 kJ mol^{-1}) (Pickering and Tobolsky 1972). Due to the relative weakness of the S–S linkage, the thermal disproportionation of organic polysulfides is a common event (Pickering et al. 1967). The same applies to polysulfide ions in solution. Although solid Na_2S_3, Na_2S_4 and Na_2S_5 were prepared in high purity and their structure was determined by X-ray diffraction (Schwarzenbach and Fischer 1960; Rosen and Tegman 1971; Weddigen et al. 1978; Brown and Battles 1984; Bittner et al. 1988), homogeneous solutions of S_3^{2-}, S_4^{2-} or S_5^{2-} are very difficult to prepare because of their rapid decomposition and establishment of various equilibria among several polysulfide species, as shown in reactions (4) and (5):

$$2\,Na_2S_5 \rightleftharpoons Na_2S_4 + Na_2S_6 \qquad (4)$$

$$S_3^{2-} + S_6^{2-} \rightleftharpoons S_4^{2-} + S_5^{2-} \qquad (5)$$

The decomposition of dimethyl tetrasulfide was shown to be a free radical reaction involving polysulfides with short chain lengths (Pickering et al. 1968). However, the mechanism of polysulfide ion decomposition in aqueous solutions is not well understood. For example, the oxidation of S^{2-}, catalyzed by transition-metal ions, is believed to be a free radical reaction (Steudel 1996), as evidenced by the fact that when S^{2-} was treated with ions such as V^{5+}, Fe^{3+} or Cu^{2+}, it was transformed to hydrosulfide radical anion, $HS^{-\bullet}$. At neutral pH values, these radicals were thought to exist as sulfur radical anions $S^{-\bullet}$ (Steudel et al. 1989). Their spontaneous decay caused the formation of S_2^{2-}. Continuation of this process gave higher polysulfide ions and finally elemental sulfur.

Individual polysulfide ions can be characterized by their UV absorption properties (Licht et al. 1986). In a study of aqueous alkali-metal polysulfide solutions containing OH^-, H^+, H_2S, HS^-, S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-} and alkali-metal cation species carried out by Licht and Davis (1997), the UV spectra were mathematically deconvoluted and the species distribution was calculated. The obvious disadvantage of this method is its complexity and the need for prior knowledge of concentrations of the original sulfur, sulfides and alkali-metal hydroxide.

Ion-pair chromatography has also been used to separate monosulfide, sulfite, and thiosulfate from polysulfides. However, polysulfide ions with four or five sulfur atoms could not be separated due to a readily established equilibrium (Steudel et al. 1989). In another ion-pair chromatographic method, the polysulfide solution was treated with KCN, the resulting S_nCN^- ions were detected and all sulfur species were distinguished (Ikeda et al. 1985). Overall, the chromatographic approach shows that it is possible to actually separate HS^-, SO_3^- and $S_2O_3^-$ from the oligomeric polysulfide species, but it was not possible to detect the individual polysulfide species themselves. The detailed species distribution present within a polysulfide solution was not visible. While this approach is useful in allowing the detection and most likely the quantification of the various species that emerge from the disproportionation of polysulfide, a fresh approach was required to allow the detailed species distribution to be visualized and quantified.

An alternative to direct observation of polysulfide ions in aqueous solution is to convert them into organic polysulfides and assay the organic species thus formed. The alkylation of polysulfide ions in aqueous solutions can be carried out either by their reactions with alkyl halides (I, Br, Cl) (Deryagina et al. 1996) or with alkyl sulfates (Shen 1999).

$$S_x^{2-} + Et_2SO_4 \rightarrow EtS_xEt + SO_4^{2-} \qquad (6)$$
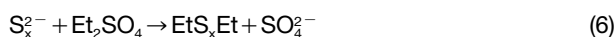
Minami and Ando (1994) have proposed the alkylation of inorganic polysulfide ions to diethyl polysulfides using diethyl sulfate [Eq. (6)], followed by detection of the resulting diethyl polysulfides by HPLC. The relative distribution of the various inorganic polysulfide ions was obtained from the HPLC peak area of the various diethyl polysulfide species. This method, however, precluded the absolute concentrations of the various polysulfide ions from being determined.

The present paper describes our efforts toward the development of a novel quantitative protocol that allows the absolute determination of various polysulfide species. It is comprised of alkylating polysulfide ions with dimethyl sulfate [Eq. (7)] followed by quantitative proton NMR spectroscopy using 1,3,5-tributyl benzene as the internal standard.

$$S_x^{2-} + Me_2SO_4 \rightarrow MeS_xMe + SO_4^{2-} \qquad (7)$$
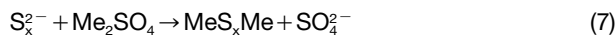
Materials and methods

^{1}H NMR spectra

^{1}H NMR spectra were acquired on a Varian 300 instrument in $CDCl_3$. High-purity sodium sulfide nonahydrate (99.9%) and dimethyl sulfate were obtained from Aldrich Chemical Co. Oxygen-free water was prepared by refluxing doubly deionized water for 2 h under a nitrogen atmosphere. 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. 1,3,5-Tri-t-butylbenzene (50 mmol L^{-1}) in $CDCl_3$ was prepared by dissolving 0.308 g (1.25 mmol) in 25 mL of degassed $CDCl_3$ using a volumetric flask. The flask was sealed with a septum and the solution kept under nitrogen. When required, aliquots of this solution were transferred using a syringe under nitrogen.

Calibration with dimethyl polysulfides

An accurate amount of a given polysulfide (for $CH_3S_3CH_3$, $CH_3S_4CH_3$) was mixed with 1.00 mL of the 0.05 mol L^{-1} solution of the internal standard in $CDCl_3$. The solution was then rapidly transferred to a 5-mm NMR tube and the spectra acquired immediately.

Synthesis of sodium disulfide Na_2S_2

Sodium sulfide nonahydrate (7.52 g, 31.2 mmol) was weighed into a 250-mL three-necked flask fitted with a reflux condenser and rubber septa. The system was flushed with nitrogen and kept under a nitrogen atmosphere. Absolute ethanol (120 mL) was transferred into the flask using a syringe. The mixture was stirred and heated in an oil bath until a homogenous solution was obtained. The solution was allowed to cool to room temperature, and then fine powdered sulfur (1.00 g) was added quickly. The resulting mixture was refluxed under nitrogen for 1 h and kept at room temperature overnight. The reflux condenser was removed and the flask connected to a water pump by a two-way glass stopper. The resulting orange solution was concentrated under vacuum to 1/3 of its original volume. The yellow precipitate was filtered in an Atmos Bag (Aldrich Chemical Co.) filled with nitrogen and dried in a round-bottom flask under high vacuum at 80 °C for 2 h. The brown-red powder was used in the following steps.

Synthesis of dimethyl tetrasulfide and other homologues

Dimethyl disulfide (0.47 mL, 5 mmol) was dissolved in 12.5 mL of $CHCl_3$ in a round-bottom flask. To this, a solution of Ph_3CS_2Cl (5 mmol) in 12.5 mL of $CHCl_3$ was added (Williams et al. 1994). The reaction flask was capped and the solution stirred for 1 h.

Then 10 mL of water was added to the reaction flask and the reaction mixture was stirred vigorously for a further 1 h. The organic layer was separated and dried with Na_2SO_4. The solvent was evaporated under reduced pressure. $CH_3S_4CH_3$ was isolated by quickly passing the residue through a column of silica gel (15 g) using pentane. $CH_3S_4CH_3$ was obtained in near-quantitative yield with a purity of approximately 90% (as determined by ¹H NMR).

By following the same procedure, dimethyl trisulfide, $CH_3S_3CH_3$, was prepared in 75% yield and dimethyl pentasulfide, $CH_3S_5CH_3$, in 88% yield. Both of these compounds were synthesized from dimethyl disulfide and Ph_3CSCl (Vorlander and Mittag 1914) or Ph_3CS_3Cl (Williams et al. 1994), respectively.

Alkylation of sodium sulfide and sodium disulfide

In a 10-mL round-bottom flask equipped with a two-way stopper and an outlet with a rubber septum, 2 mmol of $Na_2S \cdot 9H_2O$ (0.48 g) was quickly weighed, and a small stirring bar was added. The flask was purged with N_2. Then 16 mmol of NaOH (0.64 g) was dissolved in 2 mL of oxygen-free water under N_2 and the solution was allowed to cool to room temperature. This solution was then transferred, using a syringe, into the round-bottom flask containing the sodium sulfide and the mixture was stirred. To this, a solution of 0.75 mL (8 mmol) of $(CH_3)_2SO_4$ in 2 mL of internal standard solution was added drop-wise under N_2 over a period of 5 min using a syringe. Finally, the reaction mixture was stirred for another 90 min. During this time all precautions were taken to prevent evaporation of the dimethyl sulfides formed. Then the mixture was allowed to stand for 5 min and the $CDCl_3$ layer was separated and used for subsequent NMR spectral acquisition. The yield of dimethyl sulfide was calculated from ¹H NMR signal integration.

Alkylation of synthetic and industrial pulping liquors

Aliquots of 1 or 2 mL of the liquor sample were transferred into a 5- or 10-mL round-bottom flask equipped with a two-way stopper under N_2. The liquor was stirred and appropriate amounts of $(CH_3)_2SO_4$ and 0.05 mol L^{-1} internal standard in $CDCl_3$ solutions (see Tables 5 and 6) were added dropwise using a syringe over a period of 20 min. After allowing the mixture to react under stirring for another 10–20 min, the organic phase was separated and ¹H NMR spectra were acquired immediately.

Results and discussion

Quantitative ¹H NMR

Gas chromatography can be used to determine traces of dimethyl polysulfides (Wajon et al. 1985), but if substantial amounts of these species are present in a given sample, then NMR is a more suitable method. The chemical shifts of $CH_3S_xCH_3$ (x = 1–5) are well documented (Table 1) (Mott and Barany 1984; Hou et al. 2000). Figure 1 shows the ¹H NMR spectra of various pure dimethyl polysulfide species acquired on a 300-MHz spectrometer, possessing 1–5 sulfur atoms.

Figure 1   ¹H NMR of experimentally produced (bottom to top): $(CH_3)_2S_1$; $(CH_3)_2S_2$; $(CH_3)_2S_3$; $(CH_3)_2S_4$; and $(CH_3)_2S_5$. Peaks: I.S., internal standard; S_1, $(CH_3)_2S_1$; S_2, $(CH_3)_2S_2$; S_3, $(CH_3)_2S_3$; S_4, $(CH_3)_2S_4$; and S_5, $(CH_3)_2S_5$.

1,3,5-Tributyl benzene (97%, Aldrich Chemical Co.) was used as the internal standard due to its stability and because its aliphatic proton signal appears at 1.33 ppm downfield from tetramethylsilane (TMS) in $CDCl_3$. This position was chosen due to its proximity to the dimethyl polysulfide signals (approx. range 2.1–2.5 ppm). A 50 mmol L^{-1} solution of 1,3,5-tributyl benzene in $CDCl_3$ was used throughout this work.

In our efforts to arrive at a quantitative acquisition protocol, we initially determined the spin lattice relaxation times (T_1) of the protons in $CH_3S_xCH_3$ (x = 1–5) and 1,3,5-tributyl benzene, using the inversion recovery method

Table 1   Chemical shifts and spin lattice relaxation times (T_1) for MeS_xMe in $CDCl_3$.

	MeSMe	MeS$_2$Me	MeS$_3$Me	MeS$_4$Me	MeS$_5$Me
¹H NMR (ppm)	2.13	2.42	2.56	2.64	2.67
¹³C NMR (ppm)	18.02	22.03	22.54	23.17	23.83
T_1 (s)	4.63	4.54	4.28	3.90	3.56
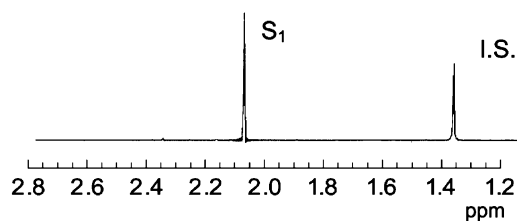
Figure 2 ^{1}H NMR of $(CH_3)_2S_1$ formed by reacting $Na_2S \cdot 9H_2O$ with $(CH_3)_2SO_4$ under basic conditions. Peaks: I.S., internal standard; and S_1, $(CH_3)_2S_1$. $(CH_3)_2S_1$ was detected at 98% purity with a reaction yield of 82%.

(Table 1). As anticipated, the T_1 values decreased with increasing number of sulfur atoms in the molecule (Table 1). Consequently, the delay time between pulses parameter (D1), of the quantitative ^{1}H NMR acquisition was set to 30 s. It was also observed that setting the acquisition time to 6 s and pulse width to 90° altered the peak area only slightly (by approx. ± 1–2%) without significant effects on the accuracy of our determinations.

To verify the reliability of the NMR measurements, a calibration was independently carried out using individual dimethyl polysulfide $CH_3S_xCH_3$ ($x = 1$–5) samples prepared from commercial dimethyl disulfide and sulfur transfer reagents (see Material and methods). It was thus verified that the ratio of the peak area of a polysulfide species to that of the internal standard (P_s/P_i) was in good agreement (± 7%) with the molar ratios of polysulfide to internal standard (M_s/M_i). This calibration showed that the systematic error of the NMR measurements was approximately ± 10%.

The alkylation reaction

Dimethyl sulfide and dimethyl disulfide have a boiling point of 39 °C and 109 °C, respectively. Consequently, the lower homologue may easily escape from the reaction mixture and may react or be absorbed by the rubber septa commonly used in oxygen-free procedures. To avoid these problems, a specially designed vessel was used to carry out the reactions. It consists of a round-bottom flask fitted with a two-way stopper connected to a glass tube with an enlarged opening for rubber septa. The two-way stopper was kept open during purging with

nitrogen and sample injection, and only then was it closed airtight. The two-way valve was aligned with the opening, allowing the syringe needle to go through it for sample and reagent introduction.

The reaction of $Na_2S \cdot 9H_2O$ with dimethyl sulfate was employed as a model to optimize the alkylation conditions. Using the procedure developed during this effort (see Materials and methods) up to 82% yield of dimethyl sulfide was obtained as a single alkylation product (Figure 2).

To arrive at the proposed protocol, we examined a number of variables in detail for their effect on the reaction. These variables were the presence of oxygen, the amount of dimethyl sulfate and NaOH, and the various modes of adding the alkylating reagent into the reaction mixture.

Effect of oxygen

In order to fully account for the effect of oxygen on the alkylation reaction of inorganic polysulfides in aqueous alkaline media, the alkylation reaction was carried out under strict oxygen-free conditions and in the presence of air (Table 2, entries 1 and 2). It was observed that in the presence of air the yield of dimethyl sulfide was 22% lower, while approximately 5% dimethyl disulfide appeared in the final product distribution. The disulfide may form via radical reactions initiated by dioxygen.

Effect of dilution of the alkylating agent

The direct addition of neat dimethyl sulfate into the reaction mixture resulted in poor yields of dimethyl monosulfide (Table 2, entry 3). To prevent high local concentrations of dimethyl sulfate, which in turn will cause serious local pH variations, the alkylating agent was added incrementally as a 4 mol L^{-1} solution in $CDCl_3$. This practice resulted in significant yield improvements, as evidenced by comparing entries 3–7 in Table 2.

Amount of sodium hydroxide and dimethyl sulfate

Throughout this effort, sodium hydroxide was added to neutralize the acid formed by the hydrolysis of dimethyl

Table 2 Alkylation yields of $Na_2S \cdot 9H_2O$ under different reaction conditions.

Entry	$Na_2S \cdot 9H_2O$ (mmol)	Water (mL)	NaOH (mmol)	O_2	$(CH_3)_2SO_4$ (mmol)	$CDCl_3$ (mL)	Reaction time (h)	Yield (%)	
								S_1	S_2
1	2	2	16	+	8	2	1.5	60	5
2	2	2	16	−	8	2	1.5	82	0
3	2	2	16	−	8	0	1.5	20	0
4	2	2	4	−	2	2	1.5	52	0
5	2	2	8	−	4	2	1.5	70	0
6	2	2	16	−	8	2	0.5	82	0
7	2	2	16	−	8	2	1.5	82	0
8	2	2	−	−	8	2	0.5	82	0
9	2	2	24	−	12	2	1.5	75	0
10	2	*	−	−	16	2	1.5	42	0
11	0.4	**	7.5	−	10.5	2	1.5	52	0

*Using 2 mL of buffer instead of water. The buffer (pH 11.98) was prepared from acetic acid (0.04 mol L^{-1}, 60.06 mL), boric acid (0.04 mol L^{-1}, 61.84 mL), phosphoric acid (0.04 mol L^{-1}, 98 mL) and NaOH (0.2 mol L^{-1}, 40 mL).
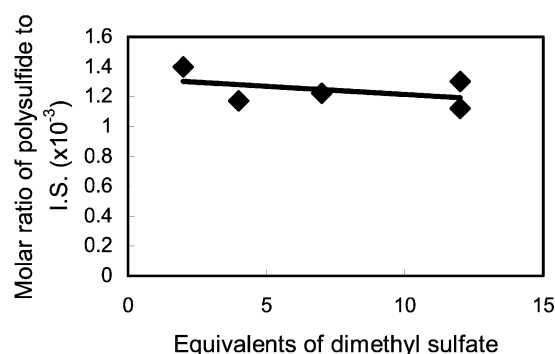**Using 0.6 mL of water and 1.4 mL of buffer.

Figure 3 The effect of the amount of dimethyl sulfate on the reaction yield. I.S., internal standard.

Figure 4 ^{1}H NMR of $(CH_3)_2S_2$ obtained by reacting Na_2S_2 with $(CH_3)_2SO_4$ under alkaline conditions. Peaks: I.S., internal standard; and S_2, $(CH_3)_2S_2$. $(CH_3)_2S_2$ was observed at 98% purity with a yield of 80%.

sulfate, to create an alkaline environment for the alkylation and to maintain high pH levels. When the dimethyl sulfate $CDCl_3$ solution (4 mol L^{-1}) was added rapidly to an aqueous solution of $Na_2S\cdot9H_2O$, the addition of extra sodium hydroxide to the reaction mixture had no influence on the yield of dimethyl sulfide (Table 2, entries 6 and 8).

Different equivalents of dimethyl sulfate were used under various experimental conditions (Table 2, entries 4, 5, 7 and 9) to determine the effect of dimethyl sulfate concentration on the yield of dimethyl sulfide. As evidenced by the plot in Figure 3, adding 2–4 equivalents of the alkylation reagent was found to be sufficient. A very large excess of dimethyl sulfate was actually found to lower the yields, probably due to saturation of the $CDCl_3$ layer by dimethyl sulfate.

Effect of reaction time and buffer

Using a 4 mol L^{-1} concentration of dimethyl sulfate, the alkylation reaction was complete within 30 min (Table 2, entries 6 and 7). If lower concentrations are to be used, longer reaction times may be necessary. In two separate runs (Table 2, entries 10 and 11) a buffer solution was used instead of water. This was carried out in order to investigate whether the reaction yields could actually be further improved. In the presence of buffer, the yield of dimethyl sulfide was reduced. This was probably due to competing reactions of dimethyl sulfate with anions present in the solution and the buffer.

Extraction efficiency

The procedure developed involves an extraction procedure that uses a volume of $CDCl_3$ equal to the volume of
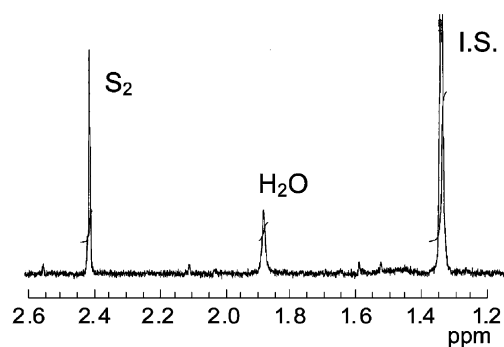
water added in the inorganic phase. A single extraction of dimethyl tetrasulfide, $(CH_3)_2S_4$, from water gave a recovery yield of more than 90%. For dimethyl sulfide, $(CH_3)_2S$, however, double extraction actually gave a somewhat lower recovery, mostly due to the high volatility of these species. Consequently, it was concluded that a single extraction should be used to avoid further dilution of the alkylated polysulfide species, which could eventually reduce the reliability of the NMR spectra. Furthermore, it was observed that saturating the inorganic phase with sodium chloride had only a negligible effect in improving the extraction efficiency.

Side reactions

During this effort we observed that disproportionation reactions of dimethyl tetrasulfide to other polysulfides were possible. The content of dimethyl tetrasulfide was found to decrease from 90% to 64% when the sample was stirred with 0.76 mol L^{-1} NaOH for 1.5 h (Table 3, run 2). However, when a $CDCl_3$ solution of dimethyl tetrasulfide was treated with NaOH (under similar conditions), the NMR spectra showed almost no difference compared to the original sample (Table 3, run 3). Adding a large excess of dimethyl sulfate to the mixture did not promote the disproportionation of dimethyl tetrasulfide (Table 3, run 4). This demonstrates that dimethyl tetrasulfide and dimethyl sulfate do not mutually react under the experimental protocol proposed. It was thus concluded that introducing $CDCl_3$ to the system at the onset of alkylation is essential in preventing side reactions.

In an effort to understand further this important variable of the alkylation, pure sodium disulfide, Na_2S_2, was

Table 3 Composition of dimethyl tetrasulfide samples subjected to different treatments.

Run	Composition (%)				
	S_2	S_3	S_4	S_5	S_6
1	0	5	90	5	0
2	2	12	64	15	7
3	0	5	90	5	0
4	0	6	89	5	0

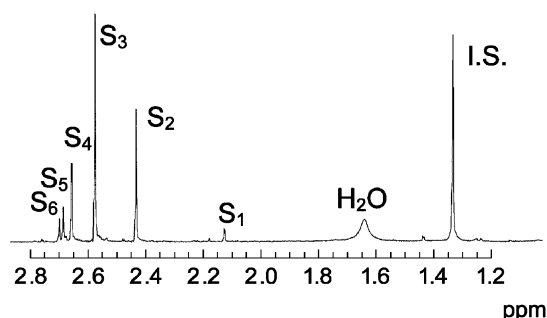Run 1: prepared by reaction of dimethyl disulfide with Ph_3CS_2Cl.
Run 2: stirred with aqueous NaOH (0.76 mol L^{-1}) for 1.5 h.
Run 3: stirred in $CDCl_3$ solution with aqueous NaOH (0.76 mol L^{-1}) for 1.5 h.
Run 4: dissolved in $CDCl_3$ and then treated with aqueous NaOH (4 mol L^{-1}) and dimethyl sulfate (8 equivalents) for 1.5 h.

Table 4 Alkylation yields of sodium disulfide aimed at optimizing the alkylation reaction.

Entry	Na$_2$S$_2$ (mmol)	Water (mL)	NaOH (mmol)	(CH$_3$)$_2$SO$_4$ (mmol)	CDCl$_3$ (mL)	Reaction time (h)	S$_2$ yield (%)
1	1.46	4.0	8.76	4.38	0	1.5	41
2	3.34	3.3	26.70	13.40	3.3	0.5	85
3	3.34	3.3	26.70	13.40	3.3	1.5	84
4	2.00	2.0	16.00	8.00	2.0	0.5	85

Figure 5 ^{1}H NMR of synthetic liquor alkylated with dimethyl sulfate under alkaline conditions; the synthetic liquor was prepared by dissolving elemental sulfur in alkaline Na$_2$S solution. Peaks: I.S., internal standard; S$_1$, (CH$_3$)$_2$S$_1$; S$_2$, (CH$_3$)$_2$S$_2$; S$_3$, (CH$_3$)$_2$S$_3$; S$_4$, (CH$_3$)$_2$S$_4$; S$_5$, (CH$_3$)$_2$S$_5$; and S$_6$, (CH$_3$)$_2$S$_6$.
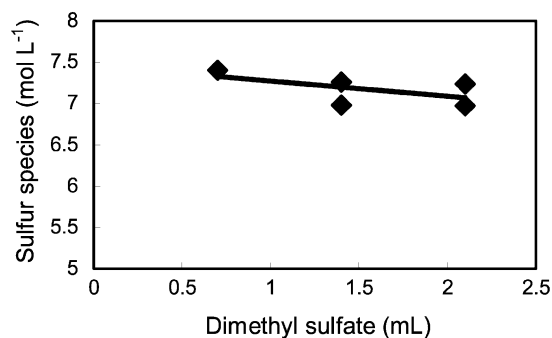
Figure 6 The effect of the amount of dimethyl sulfate used during the alkylation of synthetic liquor on the amount of total detected sulfur species.

synthesized by adding accurate amounts of sulfur to Na$_2$S in ethanol (Lee 1976) (Figure 4, Table 4). The integrity of these species under the proposed alkylation procedure was also investigated in a manner similar to that already described.
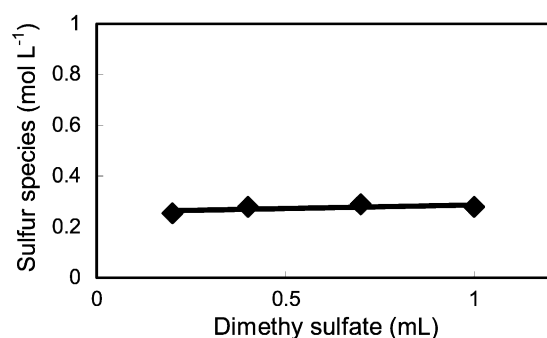
Figure 7 The effect of the amount of dimethyl sulfate used during the alkylation of industrial pulping liquor on the amount of total detected sulfur species.

This effort confirmed that adding dimethyl sulfate in the absence of CDCl$_3$ resulted in considerably lower yields (Table 4, entry 1). In the presence of CDCl$_3$, the reaction was found to be complete within 0.5 h (Table 4, entries 2 and 3), with 4 equivalents of dimethyl sulfate being sufficient to complete the alkylation (Table 4, entries 2 and 4). The optimized procedure afforded dimethyl disulfide in 85% yield. The total amount of dimethyl trisulfide and dimethyl tetrasulfide was less than 5%. This indicates that the disproportionation of Na$_2$S$_2$, if it ever took place, did not significantly interfere with the detection of S$_2$$^{2-}$ species in alkaline media.

Alkylation of industrial samples

During this effort we examined two kinds of liquor samples. The terms for these are defined as follows. "Synthetic" means laboratory-prepared polysulfide solutions obtained by dissolution of sulfur in alkaline sodium sulfide solutions. "Industrial" means *in-situ* sulfur production by oxidation of sodium sulfide. Since it was not possible to isolate the polysulfides present in such samples and investigate their reactivity individually, ensuing efforts were based on the following three assumptions: (i) all polysulfide ions react with dimethyl sulfate at a similar rate; (ii) they yield dimethyl polysulfides in similar yields; and (iii) the mode of addition of dimethyl sulfate and its amount does not change the original species equilibrium to any significant extent. Since most of these assumptions were the subject of our validation experiments, described in earlier sections of this paper, we feel confident that the species distribution of the industrial samples analyzed (provided by the alkylation reaction) truly represent their composition. A typical proton NMR spectrum of an alkylated synthetic polysulfide liquor is shown in Figure 5.

During this effort, we initially determined that the concentration of polysulfide ions in these two kinds of liquors remained nearly constant (Figures 6 and 7) while the amount of dimethyl sulfate, the reaction time and the amount of CDCl$_3$ were varied (Tables 5 and 6). The time during which dimethyl sulfate was added was 5–10 min and varying the total reaction time showed no significant effect.

The concentration of polysulfide ions was calculated from the ratio of the individual peak areas to the volumes of the inorganic and organic phases according to Eq. (8). The constant 4.5 is due to the 27 protons present in the internal standard and the 6 protons present in each dimethyl polysulfide molecule. The concentration of internal standard was kept constant at 0.050 mol L^{-1}.

$$C = P_s/P_i \times 4.5 \times 0.050 \times V_{org}/V_{ino} \qquad (8)$$

Table 5 Synthetic liquor analyses: effect of reaction variables.

Run	Volume (mL)			Reaction time (min)	Concentration (mol L^{-1})					
	Sample	$(CH_3)_2SO_4$	$CDCl_3$		S_1	S_2	S_3	S_4	S_5	S_6
1	1	0.7	2	20	0.054	0.75	0.88	0.38	0.17	0.14
2	1	1.4	2	20	0.058	0.75	0.84	0.33	0.16	0.13
2	1	1.4	2	40	0.027	0.75	0.86	0.37	0.18	0.13
3	1	2.1	2	20	0.022	0.81	0.87	0.36	0.16	0.18
5	2	2.1	6	30	0.030	0.75	0.92	0.43	0.15	0.08
Average					0.038	0.76	0.87	0.37	0.16	0.13

Table 6 Industrial pulping liquor analyses: effect of dimethyl sulfate.

Run	Volume (mL)			Concentration (mol L^{-1})				
	Sample	$(CH_3)_2SO_4$	$CDCl_3$	S_1	S_2	S_3	S_4	S_5
1	2	0.2	2	0.047	0.101	0.002	0	0
2	2	0.4	2	0.047	0.110	0.004	0	0
3	2	0.7	2	0.047	0.112	0.006	0	0
4	2	1.0	2	0.041	0.110	0.006	0	0
Average				0.045	0.108	0.004	0	0

where:

P_s: NMR peak area of the dimethyl polysulfide

P_i: NMR peak area of the internal standard

V_{org}: volume of the organic phase

V_{ino}: volume of the inorganic phase

A challenge in the analysis of industrial samples is that the sulfur concentration needed to select the amount of reagents to be used is often unknown. During this effort we were guided by the color changes induced in the polysulfide solutions and used these as indicators of reaction completion. Polysulfide ions, with the exception of the monosulfide, are orange or yellow solutions and the color intensity is proportional to their concentration. Discoloration during alkylation was found to be a reliable indicator of reaction completion, indicating that enough dimethyl sulfate had been added. At this point we should mention the fact that previous work done on the calculation of the expected species distribution of polysulfide solutions (Licht and Davis 1997) has generally shown that disulfide should not exist under the pH conditions existing in synthetic liquors and the amounts of penta- and hexa-sulfide species would be very low. Our work appears to contradict these conclusions. To this effect we cite data in Table 4 showing that the model sodium disulfide alkylated with excess sodium hydroxide was stable. However, our continuing efforts in this area are currently focused on identifying the underlying science behind these discrepancies.

Conclusions

Overall, the results of this work led to the conclusion that the method described can be used for the efficient and reliable quantitative detection of polysulfide ions present in alkaline solutions. The protocol developed could be particularly useful in promoting our understanding of the intricate and delicate chemistry of polysulfide equilibria.

Acknowledgements

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