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Sulfur Stable Isotope Distribution of Polysulfide Anions in an $(NH_4)_2S_n$ Aqueous Solution

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Methylation of polysulfides $[(NH_4)_2S_n)]$ by reaction with CF_3SO_3-CH_3 followed by separation of the produced dimethylpolysulfides by liquid chromatography and subsequent highly accurate stable isotope analysis by a continuous-flow isotope ratio mass spectrometer shows that polysulfide anions in an aqueous solution exchange isotopes with the other sulfur species in the system. It demonstrates for the first time that polysulfide anions are ^{34}S-enriched in equilibrium relative to total sulfur as a function of their sulfur chain length.

Inorganic polysulfides (S_n^{2-}) play an important role in many fields of the chemical industry, environmental science, and geochemistry.[1−6] Numerous methods have been developed in order to study the speciation and equilibrium constants of polysulfide ions.[7−13] However, no attention was given to the stable isotope ratio $^{34}S/^{32}S$ ($\delta^{34}S$) distribution of polysulfides in aquatic media because of technical difficulties in both accurate measurement of the isotopic ratio and isolation of the polysulfide anions from the complex polysulfide solution without altering it during analysis.

The aqueous polysulfide solution is a complex mixture of species that are composed of H_2S, HS^-, S^0, and S_n^{2-} ($n = 2-8$) and their protonated forms. The distribution of these species depends on the pH and the saturation degree of the aqueous solution. Recently, a new approach for polysulfide speciation using methyl trifluoromethanesulfonate (methyl triflate) was proven to be an efficient and reliable method for fast methylation followed by high-performance liquid chromatography (HPLC) quantification of the stable dimethylpolysulfides.[13] Application of the method showed that the tetra-, penta-, and heptasulfides are the most dominant polysulfide species under sulfur supersaturation conditions.

Highly accurate $\delta^{34}S$ measurements (±0.3‰) of these polysulfides can be achieved by continuous-flow isotope ratio mass spectrometry (CF-IRMS).

The combination of these two methods was employed in this study to follow the distribution and isotope mixing of the polysulfide species obtained at equilibrium in aquatic conditions.

Polysulfides were produced by reacting elemental sulfur S_8^0 with aqueous ammonium polysulfides $(NH_4)_2S$ (ambient temperature in glovebox <0.3% O_2) according to the following simplified equation:

$$nS^0 + xS^{2-} \rightleftarrows S_{n+x}^{\ \ 2-} \tag{1}$$

We used 25 mmol of S^0 and 25 mmol (or 2.5 M) of $(NH_4)_2S$ to reach the overall stoichiometric polysulfide ratio of $(NH_4)_2S_2$. The orange polysulfide solution was stirred for at least 1 h to reach equilibrium. At our working pH range (8.5−9.0 buffered by the ammonia solution), most of the sulfide species is in the bisulfide form (HS^-). There is a negligible concentration of the monoanion HS_n^-, and the dominant species is the dianion S_n^{2-}.[14] The $(NH_4)_2S_2$ solution diluted in water into 0.1 M, and the solution reacted with methyl triflate, which methylated the polysulfides according to eq 2.

$$S_n^{\ 2-} + 2CF_3SO_3CH_3 \rightarrow (CH_3)_2S_n + 2CF_3SO_3^{\ -} \tag{2}$$

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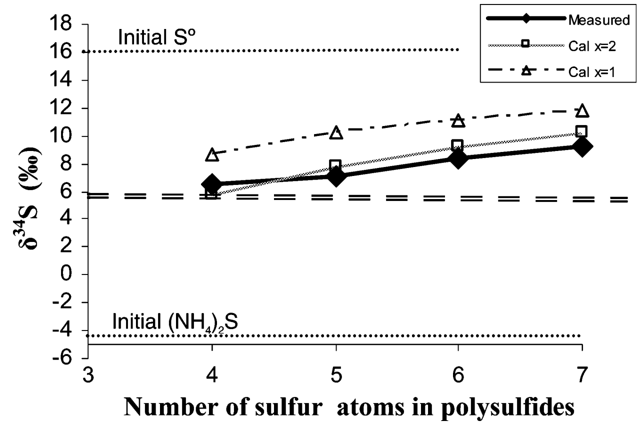

Figure 1. $\delta^{34}S$ of the isolated Me_2S_n derivatives of polysulfide anions. The bold broken line is the mass-balance value of total sulfur (eq 3). The thin lines represent the initial $\delta^{34}S$ values of S^0 and $(NH_4)_2S$.

The clear solution of dimethylpolysulfides was immediately extracted with pentane, concentrated by a rotor evaporator at ambient temperature, and introduced into a reversed-phase chromatography column (silica gel, C-18 stationary phase) using a mixture of $HCOOH/CH_3CN$ (0−10% CH_3CN) as the eluent. The distribution of the polysulfides (Me_2S_2−Me_2S_7) was determined by reversed-phase HPLC calibrated by the method previously reported.[15]

The distribution of polysulfides was in good agreement with speciation calculations using the thermodynamic data of ref 13 and taking into account the fact that the solution is undersaturated with respect to sulfur. Details of the observed and calculated polysulfide distributions are depicted in Table S1 and Figure S1 in the Supporting Information.

The eluted fractions were extracted with pentane and concentrated. We were able to isolate Me_2S_4−Me_2S_7 in quantities sufficient for IRMS analysis with purity that ranged between 90 and 96%.

The initial $\delta^{34}S$ values of the sulfide (−4.4‰) and the elemental sulfur (16.1‰) were determined, and the stoichiometric isotope value was calculated according to the Rayleigh isotope mass-balance equation for a closed system:

$$\delta_T = x\delta_{S^{2-}} + (1-x)\delta_{S^0} \tag{3}$$

δ_T represents the stoichiometric $\delta^{34}S$ value (of the total sulfur), and x represents the mole fraction of the precursor components (sulfide and elemental sulfur) for the formation of polysulfides. According to eq 3, δ_T for this polysulfide solution is 5.85‰. Direct precipitation of the polysulfide solution by an $AgNO_3$ solution yielded almost the same value, 5.9‰. The accuracy of this method for total sulfur (δ_T) analysis is ±0.5‰.[16]

The $\delta^{34}S$ values of the isolated Me_2S_n ($n = 4-7$) are presented in Figure 1.

The results show a slight ^{34}S enrichment of the polysulfides as compared to the mixing line or total sulfur in the solution. As the number of sulfur atoms in the polysulfides increases, the ^{34}S enrichment increases up to 3.4‰ in S_7. It has been shown in the past that isotopic exchange takes place using radiolabeled sulfur isotopes (^{35}S).[17] However, because of the relatively large analytical error (>1% or 10‰) of that method, which is more than 1 order of magnitude higher than that of our method, it was impossible to ascertain the small but pronounced ^{34}S enrichment as observed in the present study.

There are two approaches to explain this ^{34}S enrichment as a function of the polysulfide chain length. The first approach is related to the fact that practically all elemental sulfur (of oxidation state 0) is in the polysulfide anion form under the pH range and degree of sulfur undersaturation that we work (8.5−9.0). The polysulfide forms can be presented as follows: $^{-}S\mathbf{S}_nS^{-}$ or $\mathbf{S}_{n+1}S^{2-}$. If we assume that there is an isotopic "memory" of each species (S^0 or HS^-) and that no isotopic exchange occurs between the middle part of the polysulfide chain (S^0) and HS^-, then we can apply the following equation to predict what the $\delta^{34}S$ of the polysulfides should be as a function of their sulfur chain length:

$$\delta_{S_{x+n}{}^{2-}} = (x\delta_{S^{2-}} + n\delta_{S^0})/(x+n) \tag{4}$$

where x is the number of (negatively charged) sulfide sulfurs in the polysulfide chain and can get the values of 1 or 2 as discussed above. n represents the number of S° atoms in the middle polysulfide chain. The results of these calculations are presented in Figure 1 for $x = 1$ and 2. The calculated line for $x = 2$ is similar to that of the measured values although a little ^{34}S-enriched. According to this, there is a possibility that there is indeed isotopic memory of S^0 and HS^- in the polysulfide solution. However, this phenomenon can be explained by another mechanism that involves full isotopic exchange between the species if we take into account the difference in the bond strength between $^{32}S-^{34}S$ and $^{32}S-^{32}S$. According to quantum mechanics, the heavier isotope forms a stronger bond and therefore will tend to cleave less than the lighter isotope. Such cleavage and formation of S−S bonds during dynamic equilibrium between the species in the polysulfide solution will eventually enrich the polysulfides with ^{34}S compared to the hydrogen sulfide species. Moreover, the middle sulfur atoms participate in two sulfur−sulfur bonds, while the end sulfurs participate in only one such bond, which by the same reasoning leads to the conclusion that the middle sulfur atoms are enriched by the ^{34}S atoms. As the polysulfide chain becomes longer, the probability of ^{34}S is correspondingly increased, which can explain our observations.

To distinguish between these two explanations, we performed another experiment and used S^0 and $(NH_4)_2S$ with different $\delta^{34}S$ values. In this experiment, $(NH_4)_2S$ is ^{34}S-enriched (34.5‰) and S^0 is much lighter (−1.5‰). According to eq 2, the calculated values of the polysulfides should be ^{34}S-depleted compared to the total sulfur line, and as the polysulfide chain length increases, $\delta^{34}S$ should become lighter.

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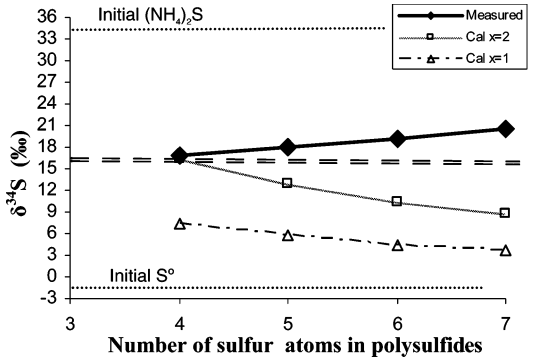

Figure 2. $\delta^{34}S$ of the isolated Me_2S_n derivatives of polysulfide anions. The broken line represents the mass-balance value of total sulfur (eq 3). The thin lines represent the initial $\delta^{34}S$ values of S^0 and $(NH_4)_2S$.

The results presented in Figure 2 show the same ^{34}S-enrichment phenomenon as that in the first experiment. Therefore, it is clear that there is full isotopic exchange between the species in the polysulfide solution, and there is no isotopic memory of the origin of each sulfur species. This is in line with our previous report that the characteristic time for polysulfide disproportionation is <10 s.[18] Moreover, the ^{34}S enrichment of the polysulfides is almost the same in the two tests, which supports the second approach.

A simple mass balance, taking into account the atomic fraction of the sulfur in each form of the polysulfide (y_{S_n}) and atomic fraction of sulfur in the sulfide form (y_{HS^-}), allows calculation of the isotope enrichment of hydrogen sulfide (δ_{HS^-}).

$$\delta_{HS^-} = \frac{\delta_T - \sum_{n>1}(\delta_{S_n} y_{S_n})}{y_{HS^-}} \qquad (5)$$

Our calculations, taking into account the theoretical distribution of polysulfides and the observed enrichments of the different polysulfides (and neglecting the small contributions of the $n = 2$, 3, and 8 species), show that $\delta_{HS^-} = 3.2$ and 13.8‰ for the first and second tests, respectively. This implies enrichment of −2.8 and −2.7‰ compared to δ_T. Theoretical calculations indicated enrichment in ^{34}S of elemental sulfur relative to H_2S by 3‰ at 25 °C based on chemical equilibrium between the species.[19] More support for these results obtained by acidification experiments[16] of similar $(NH_4)_2S_2$ solutions that released $H_2S(g)$ and S_8^0 according to the following equation:

$$S_n^{2-}(aq) + 2H^+(aq) \rightarrow xH_2S(g) + (n-x)S^0(s) \qquad (6)$$

$\delta^{34}S$ of the released elemental sulfur and hydrogen sulfide showed that the $\delta^{34}S$ values of the elemental sulfur are always ^{34}S-enriched by about 4‰ compared with the trapped H_2S and about 1.5‰ relative to the calculated $\delta^{34}S$ of the polysulfide solution (i.e., total sulfur). Because the origin of the released elemental sulfur from the solution is the polysulfides, it can support the polysulfide enrichment relative to the sulfide in the solution.

In conclusion, by employing state-of-the-art methods involving “freezing” polysulfide anions out of an aqueous solution and subsequent highly accurate stable isotope analysis (CF-IRMS), we were able to prove for the first time that the polysulfides are ^{34}S-enriched by equilibrium relative to total sulfur as a function of the sulfur chain length.

The results further indicate that the sulfur isotopes in the middle of the catenated sulfur chains are enriched by S^{34} compared to the sulfur located at the two ends of the chain. We speculate that despite a rather rapid self-exchange of sulfur positions within the polysulfide chain the heavy isotopes tend to spend more time in the middle of the chain, where they can participate in two $S^{34}-S^{32}$ bonds.

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Supporting Information Available: Experimental data and the observed and calculated polysulfide distributions are depicted in Table S1 and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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