

## Analysis and Equilibrium Constant of Polysulfides in Desulfurization Solution

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Polysulfides play key roles to thorough understanding of the desulfurization mechanism. The analysis and equilibrium constant of polysulfides from dissolved sodium sulfide and inorganic sulfur has been studied. Polysulfides with different chain length are prepared. The influence of absorption wavelength, pH value and other components in the desulfurization solution on the determination of polysulfide concentration by UV spectrophotometry is investigated. The optimum absorption wavelength of polysulfide is 285 nm. The molar extinction coefficient is  $1,458 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . Using the proposed UV spectrophotometric, the polysulfide concentration in PDS desulfurization solutions is determined under different the total amount of divalent sulfur and the total amount of zero valent sulfur. In addition, the total negative bivalent sulfur is measured by the iodimetry method. The activity coefficients of all ions are calculated by the Debye-Huckel law. At 80 °C, The calculated average chain length of polysulfides is 5.64. The equilibrium constant of the polysulfide with elemental sulfur and polysulfide in the desulfurization solution is 9.362.

### 1. Introduction

Phthalocyanine cobalt sulfonate (PDS) desulfurization, one of wet desulphurization methods, is widely used in a variety of industrial gas desulfurization process. In the process of wet desulphurization, part hydrogen sulfide in the gas streams turn into undesired secondary salts in the desulfurization solution, such as sulfite, sulfate, thiosulfate, etc. The secondary salts reduce desulfurization efficiency. Thus, some desulfurization solution has to be discharged regularly to avoid second salts accumulation. It is costly to treat discharged desulfurization solution to meet the environmental protection constraint.

Studel (1996) show that polysulfides play an important role in the formation of secondary salts. In the desulfurizing liquid,  $\text{HS}^-$  react with elemental sulfur to form disulfide. Disulfides and elemental sulfur react to form polysulfides. Meanwhile, polysulfides are oxidized to form elemental sulfur, thiosulfate, sulfite and sulphate (Van den Bosch et al., 2008). Therefore, the study of polysulfides is a more in-depth understanding of the desulfurization mechanism, and helpful to decrease discharge of the desulfurization solution.

For polysulfides, many researchers proposed different analysis methods. Zhang (2006) determined the polysulfides used the EDTA capacity. This method need to go through a number of washing steps, and the  $\text{HS}^-$  effects the results. Kamyshny (2004) used high performance liquid chromatography (HPLC) to determine polysulfides in the solution. The standards were self-made and chromatographically separated, which is time-consuming. Deng (1997) used DU-650 ultraviolet spectrophotometer determine disulfide at 276 nm with cyclohexane as reference. For the polysulfide of biological desulfurization process, Kleinjan (2005) used spectrophotometric method at 285 nm. In the above methods, UV spectrophotometry (Danielsson et al., 1996) is simple and rapid, easy to be applied in the factory.

On equilibrium reaction of the polysulfides in the desulfurization solution, Kleinjan (2005) measured equilibrium constant of  $9.10 \pm 0.08$  (at 21 °C),  $9.17 \pm 0.09$  (at 35 °C). The average length of the sulfur chain was  $4.91 \pm 0.32$  (at 21 °C) and  $4.59 \pm 0.31$  (at 35 °C). Teder (1971) measured a constant  $\text{pK}_x$  of 8.82 (at 25 °C) and 9.15 (at 80 °C). The polysulfide chain length is 4.4 (25 °C) and 5.0 (80 °C). But for PDS desulfurization system has not been

studied. In this paper, the content of polysulfide in PDS desulfurization solution is determined by UV spectrophotometry. The average chain length and equilibrium constant of polysulfide are calculated.

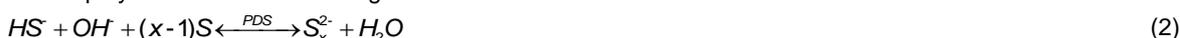
## 2. Experimental principle

Substance or ion absorbs light in a wavelength range. At a certain wavelength, the relationship between absorbance and its content follows Lambert-Beer's law (Rickard, 2007):

$$A = Kbc \quad (1)$$

$A$  is the absorbance,  $K$  is the molar absorption coefficient, which is related to the nature of the absorbing material and the wavelength  $\lambda$  of the incident light.  $c$  ( $\text{mol} \cdot \text{L}^{-1}$ ) is the concentration of light-absorbing material,  $b$  is the thickness of the absorption layer (cm).

$\text{HS}^-$  and elemental sulfur to generate polysulfide equation is as follows, PDS play a catalytic role (Teder, 1971),  $x$  is the polysulfide sulfur chain length:



The negative bivalent sulfur ions in the desulphurization solution are in the form of negative divalent sulfur ions, dissolved hydrogen sulfide molecules,  $\text{HS}^-$  ions and  $\text{S}^{2-}$  ions in the polysulfide. Therefore, the expression of all negative divalent sulfur ions in the desulfurization solution is expressed by the Eq(3).

$$[\text{S}^{2-}]_{\text{total}} = [\text{S}^{2-} \text{ in } \text{S}_x^{2-}]_{\text{total}} + [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}] \quad (3)$$

The negative bivalent sulphide concentration in the polysulfide refers to the concentration of negative divalent sulfur ions in all polysulfides:

$$[\text{S}^{2-} \text{ in } \text{S}_x^{2-}]_{\text{total}} = [\text{S}_2^{2-}] + [\text{S}_3^{2-}] + \dots + [\text{S}_{x_{\text{max}}}^{2-}] \quad (4)$$

The zero-valent sulfur concentration in polysulfides refers to the concentration of zero-valent sulfur in all polysulfides .

$$[\text{S}^0 \text{ in } \text{S}_x^{2-}]_{\text{total}} = [\text{S}_2^{2-}] + 2[\text{S}_3^{2-}] + \dots + (x_{\text{max}} - 1)[\text{S}_{x_{\text{max}}}^{2-}] \quad (5)$$

The polysulfide ions in the desulfurization solution are mainly  $\text{S}_6^{2-}$ ,  $\text{S}_5^{2-}$  and  $\text{S}_4^{2-}$ . In the medium alkaline solution  $\text{pH} > 14$ , the solution is mainly in the form of  $\text{S}_3^{2-}$  and  $\text{S}_2^{2-}$ . The average chain length is calculated by the following equation:

$$x = \frac{[\text{S}^0 \text{ in } \text{S}_x^{2-}]_{\text{total}}}{[\text{S}^{2-} \text{ in } \text{S}_x^{2-}]_{\text{total}}} + 1 \quad (6)$$

Substituting Eq(3) into the above equation:

$$x = \frac{[\text{S}^0 \text{ in } \text{S}_x^{2-}]_{\text{total}}}{[\text{S}^{2-}]_{\text{total}} - [\text{H}_2\text{S}] - [\text{HS}^-] - [\text{S}^{2-}]} + 1 \quad (7)$$

Therefore, the equilibrium constant  $K_x$  is calculated by Eq (8):

$$K_x = \frac{[\text{S}_x^{2-}][\text{H}^+]}{[\text{HS}^-]} \times \frac{\gamma_{\text{S}_x^{2-}} \gamma_{\text{H}^+}}{\gamma_{\text{HS}^-}} \quad (8)$$

Total sulfur in the desulfurization solution can be determined by iodometric analysis of concentration values (Chen, 1995). Using the UV spectrophotometric method determine  $[\text{S}^0 \text{ in } \text{S}_x^{2-}]_{\text{total}}$ . The concentration of dissolved hydrogen sulfide in the desulfurization solution can be calculated by Henry's equation, and then the corresponding concentration of hydrogen sulfide ion and sulfur ion are obtained according to the two-stage ionization equilibrium constant of hydrogen sulfide in the aqueous solution. Finally, the average chain length of polysulfide can be calculated by Eq(6).

The equilibrium between the hydrogen sulfide concentration and the hydrogen sulphide partial pressure can be described by the Henry's constant  $H_{\text{H}_2\text{S}}$  ( $\text{Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ ). At a constant pressure and a sufficiently low concentration of hydrogen sulphide, it can be expressed as:

$$P_{\text{H}_2\text{S}} = H_{\text{H}_2\text{S}}[\text{H}_2\text{S}] \quad (9)$$

Henry's constant of hydrogen sulfide, the expression is as follows (Cheng et al., 2016).

$$\ln H_{\text{H}_2\text{S}} = \frac{B_1}{T} + B_2 \ln T + B_3 T + B_4 \quad (10)$$

$B_1 = -13,236.8$ ,  $B_2 = -55.0551$ ,  $B_3 = 0.0595651$ ,  $B_4 = -342.595$ . The units of  $H_{H_2S}^I$  and  $H_{H_2S}$  are different, the conversion formula is as follows.

$$H_{H_2S} = \frac{1.01325 \times 10^5}{\rho_w} H_{H_2S}^I \quad (11)$$

The two-stage ionization equilibrium constant for hydrogen sulfide in aqueous solution is given below:

$$K_1 = \frac{[HS^-][H^+]}{[H_2S]} \times \frac{\gamma_{HS^-} \gamma_{H^+}}{\gamma_{H_2S}} \quad (12)$$

$$K_2 = \frac{[S^{2-}][H^+]}{[HS^-]} \times \frac{\gamma_{S^{2-}} \gamma_{H^+}}{\gamma_{HS^-}} \quad (13)$$

In the eq (12) and (13):  $K_1 = 1.1 \times 10^{-7}$ ,  $K_2 = 1.3 \times 10^{-13}$  (Edwards et al., 1978).

The activity coefficient can be calculated using Debye-Huckel law, For component  $i$ , the activity coefficient  $\gamma_i$  is expressed as follows:

$$\log \gamma_i = -\frac{z_i^2 A \sqrt{I}}{1 + \beta a_i \sqrt{I}} \quad (14)$$

In the formula (14),  $\gamma_i$  represents the activity coefficient of the component  $i$ ,  $z_i$  represents the charge number, and  $I$  represents the ionic strength of the solution. The ionic strength  $I$  ( $\text{mol} \cdot \text{L}^{-1}$ ) has the following expression, where  $[i]$  is the concentration of the component  $i$ .

$$I = \frac{1}{2} \sum z_i^2 [i] \quad (15)$$

### 3. Experimental reagents and instrument

#### 3.1 Reagents

Sodium sulfide nonahydrate (AR), sodium thiosulfate pentahydrate (AR), sodium carbonate anhydrous (AR), sodium sulfite anhydrous (AR), sodium sulfate anhydrous (AR), PDS, sodium thiocyanate (AR) and sodium hydrogen carbonate are purchased from Tianjin Bodi Chemical Industry Co., Ltd.

Preparation of deoxygenated water: Take a certain amount of deionized water, use a heating mantle heated to boil, in the case of boiling 10 min, sealed, cooled to room temperature.

Plant desulfurization liquid composition: the concentration of sodium carbonate, sodium bicarbonate, sodium thiocyanate, sodium thiosulfate, sodium sulphite, sodium sulfate and PDS are  $5.5 \text{ g} \cdot \text{L}^{-1}$ ,  $22.87 \text{ g} \cdot \text{L}^{-1}$ ,  $10.649 \text{ g} \cdot \text{L}^{-1}$ ,  $100 \text{ g} \cdot \text{L}^{-1}$ ,  $7.025 \text{ g} \cdot \text{L}^{-1}$ ,  $8.192 \text{ g} \cdot \text{L}^{-1}$ ,  $0.035 \text{ g} \cdot \text{L}^{-1}$ .

#### 3.2 Instrument

Eyelaosb-2100 Oil bath with stirrer, Shanghai Yuejin medical equipment factory; 1800 UV-visible spectrophotometer with quartz absorption cells (the path lengths are respectively 1 cm and 0.5 mm), Mapada Co., Ltd in Shanghai.

### 4. Experimental procedure

The three-neck flask is purged with nitrogen for 5 min. According to the proportion, the required amount of sodium sulfide, elemental sulfur and 250 mL deoxygenated water are added to the three-necked flask. Adjust the reaction temperature to  $90 \text{ }^\circ\text{C}$ , continue to slowly purge nitrogen. Stirring until the elemental sulfur completely dissolved.  $0.1 \text{ mol} \cdot \text{L}^{-1}$  NaOH is prepared with deoxygenated water for the dilution of polysulfide. Using UV spectrophotometry to measure the total concentration of zero valent sulphur atoms in polysulfide ions.

### 5. Results and discussion

#### 5.1 Preparation of Sodium Polysulfide

With the chain length increase, the color is deepened. When the chain length is less than or equal to 5, the reaction product is a homogeneous solution. When the chain length is greater than 5, part elemental sulfur cannot be dissolved into a suspension. This is consistent with Xia (1994). The next step in this work, only sodium disulfide to sodium pentasulfide solutions are used.

## 5.2 Wavelength selection

Disulfide to five sodium sulfide solutions are diluted with 0.1 mol L<sup>-1</sup> NaOH solution. The spectra are shown in the Figure 1.

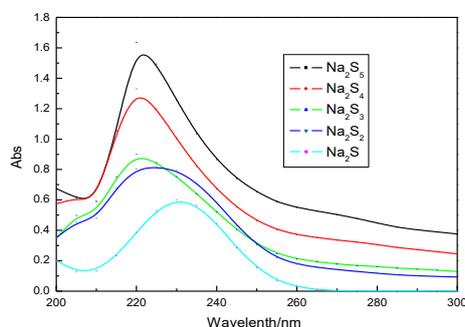


Figure 1: Different sodium polysulfide's spectrum

As seen from Figure 1, polysulfide maximum absorption peak (230nm) is overlapped with sodium sulfide. In order to eliminate sodium sulfide interference, the determination of wavelength should be selected after 280 nm. In addition to sulfide polysulfide solution, there are other water-soluble components including sodium carbonate, sodium bicarbonate, sodium thiocyanate, sodium thiosulfate, sodium sulphite, sodium sulfate and PDS. The spectrum of components is shown in Figure 2.

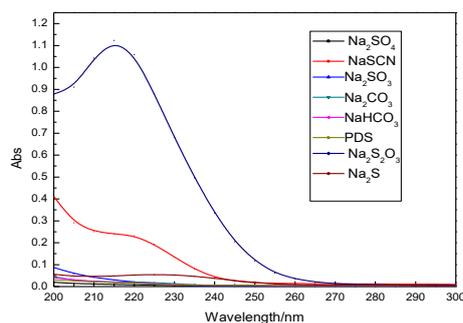


Figure 2: Spectrum of other components in desulfurization solution

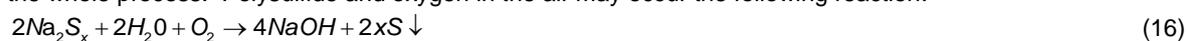
It can be seen from Figure 2, after 280 nm, the water-soluble components have no effect on the determination of polysulfide.

Deng (1997) used 276 nm, but not suitable for PDS desulfurization solution polysulfide measurement. Kleinjan (2005) used a wavelength of 285 nm to analyze the polysulfide concentration. As can be seen from Figures 1 and 2, for the PDS desulfurization solution, the measurement of the polysulfide is performed at a wavelength of 280 nm or more. In order to compare with Kleinjan's work, choosing 285 nm as the measurement wavelength.

## 5.3 Effect of pH on Analysis

Using different NaOH solution dilutes the polysulfide. The results show that when the chain length is less than or equal to 4, pH values do not affect the measurement. For pentasulfide, when the pH value is greater than or equal to 11, the solution is clarified.

In the dilution process, the solution inevitably contacts with a small amount of air even if careful deaeration in the whole process. Polysulfide and oxygen in the air may occur the following reaction:



Suspension of sulfur is occurred in the solution. Therefore, using NaOH as diluent can effectively limit the production of suspended sulfur during the dilution process.

#### 5.4 Determination of standard curve

At 285 nm, the sodium disulfide to sodium pentasulfide is diluted from 13 to 300 times with 0.1 mol·L<sup>-1</sup> NaOH solution. The resulting standard curve is shown in Figure 3.

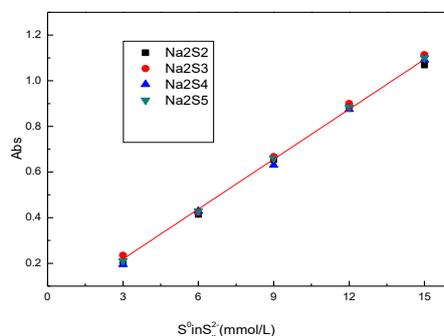


Figure 3: Standard curve of different sodium polysulfides

The standard curve obtained in Figure 3 is:  $A = 0.07292 \times \frac{[S^{2-}]_{total}}{[S^0 \text{ in } S_x^{2-}]} \cdot \frac{[S^{2-}]_{total}}{[S^0 \text{ in } S_x^{2-}]}$  (mmol·L<sup>-1</sup>) is the concentration of sodium polysulfide, the correlation coefficient is 0.99951. The standard curve slope of sodium polysulfide is 0.07292. The value of the molar extinction coefficient is 1,458L·mol<sup>-1</sup>·cm<sup>-1</sup>.

#### 5.5 Determination of sodium polysulfide in PDS desulfurization solution

At 85 °C, a set of four mixtures is made of dialyzed sulphur suspension and deaerated sodium sulphide nonahydrate. The total sulfur concentration is 31.25 mmol·L<sup>-1</sup>. The total sulfide concentrations vary from 2.17 to 8.17 mmol·L<sup>-1</sup>. When equilibrium is reached, the polysulfide excess sulfur concentrations are measured, as well as pH values. Dates are reported in Table 1.

Table 1: Experimental data

[S <sup>2-</sup> ] <sub>total</sub> (mmol·L <sup>-1</sup> )	[S <sup>0</sup> inS <sub>x</sub> <sup>2-</sup> ] (mmol·L <sup>-1</sup> )	pH
2.17	5.869	9.45
5.17	11.849	9.25
6.67	20.049	9.51
8.17	21.777	9.35

At the experimental pH range, the H<sub>2</sub>S and S<sup>2-</sup> concentrations are negligible.

$$[HS^-] = [S^{2-}] - [S_x^{2-}] \quad (17)$$

Combining Eq(7), (8) and (17) to Eq(18):

$$[H^+] \times \frac{\gamma_{S_x^{2-}} \gamma_{H^+}}{\gamma_{HS^-}} = (x-1) K_x \frac{[S^{2-}]_{total}}{[S^0 \text{ in } S_x^{2-}]} - K_x \quad (18)$$

Draw the following Figure 4 according to Table 1. It can be seen from Figure 4, pK<sub>x</sub> = 9.362, average polysulfide chain length x = 5.64. The value is greater than Kleinjan (2005), but almost equal with Teder (1971). The difference is possible that Kleinjan measures a biological desulfurization solution. Organic sulfur has a smaller particle size and hydrophilicity which makes it and inorganic sulfur different.

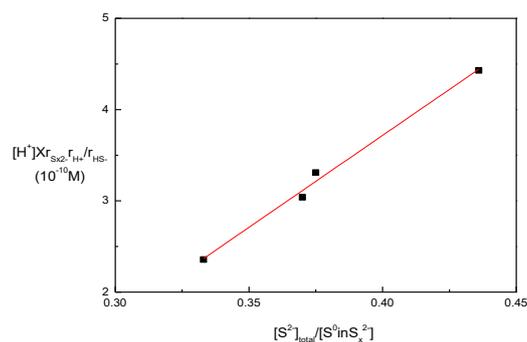


Figure 4: Linearization of the equilibrium data

## 6. Conclusion

The polysulfide measurement and calculation method proposed in this paper is simple and reliable. It can be applied to practical industrial production. Since sulfides and polysulfides are susceptible to oxidation, oxygen is carefully removed during the analysis and use small light path. In the next step, the effect of polysulfide concentration and chain length on the amount of secondary salt in the process of oxidative regeneration of desulfurization solution will be studied. The optimum process conditions will be found to minimize the secondary salt and reduce the discharge of desulfurization solution. And its impact on the environment to a minimum.

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