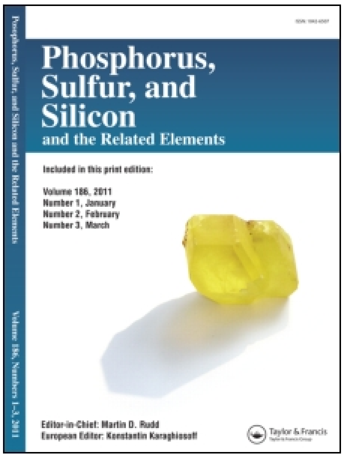

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Studies on the Chemistry OF H_2S and H_2S_x in Liquid Sulfur

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STUDIES ON THE CHEMISTRY OF H_2S AND H_2S_x IN LIQUID SULFUR

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Abstract The kinetics of removal of H_2S and H_2S_x from liquid sulfur using air sparging and amine catalysts is discussed. Removal by air is suggested to occur by reaction of O_2 with H_2S and H_2S_x both in solution and in the headspace above the liquid sulfur forming S_8 and SO_2. The SO_2 so formed likely reacts with H_2S/H_2S_x. Treatment of liquid sulfur containing H_2S/H_2S_x with amines results in sulfur containing no polymeric sulfur. This is believed to occur by proton abstraction from H_2S_x and decomposition of the resulting HS_x^- anion to S_8 and eventual formation of H_2S.

INTRODUCTION

Elemental sulfur is made industrially by oxidation of H_2S in a two-step process involving partial combustion in a front-end furnace to sulfur, SO_2 and water and reaction of further H_2S with the SO_2 over an alumina catalyst in a series of convertors [1]. Overall, this process can be made to operate at efficiencies of >99%. Despite this high efficiency, the liquid sulfur product contains residual H_2S which is present as dissolved gas and combined as H_2S_x in the following equilibrium:

$$H_2S + S_8 \rightleftharpoons H_2S_x \qquad ...(1)$$

Solidification of the sulfur results in some loss of H_2S but approximately 50% remains trapped in the solid. In order to facilitate handling of the solid, it is becoming normal practice to de-gas the liquid sulfur prior to solidification. Sparging with air with or without the addition of amine catalysts is the method most often adopted by industry [2]. This study reports data on the kinetics of H_2S/H_2S_x removal using air and amine degassing and the effect of these processes on the properties of the sulfur.

EXPERIMENTAL

Liquid sulfur containing H_2S and H_2S_x up to 200 ppmw was prepared by bubbling H_2S through pure sulfur at 140°C for 5 - 60 minutes and then storing the liquid at 140°C for 12 h. This storage period allows equilibration of H_2S with S_8 to form H_2S_x. At 140°C the H_2S/H_2S_x ratio is approximately 2:1 and is similar to the ratio observed for the collective production of an industrial sulfur plant [2].

Degassing experiments were conducted by passing air or nitrogen (800 mL/min) through liquid sulfur (1 L) stirred at 1500 rpm thermostated at 140°C in a 2 L beaker fitted loosely with a Teflon lid. Samples of liquid sulfur were removed at 5 minute intervals and were analyzed for H_2S and H_2S_x content using FTIR. Details of this analysis have been published elsewhere [2]. In the experiments where amine catalysts were used, these substances (Table 1) were added immediately prior to starting the stirrer. Under the conditions of these studies, dissolved H_2S was removed very rapidly. A first order plot of H_2S_x removal gave a linear relationship from which $t_{1/2}$ for H_2S_x decomposition was calculated.

RESULTS AND DISCUSSION

Table 1. Degassing of Liquid Sulfur by Air Sparging and with Amine Catalysts

Sparge Gas	S_8 Temperature (°C)	Catalyst	t ½ (min)
N_2	142	None	461
N_2	140	Morpholine (10 ppmw)	8
N_2	140	Quinoline (10 ppmw)	29
Air	142	None	26

Data in Table 1 show that air sparging resulted in removal of H_2S_x at a much faster rate than sparging with N_2. Observation of H_2S and SO_2 in the headspace gases indicates that some oxidation of either H_2S or H_2S_x occurred. Although difficult to quantify, it was clear that both H_2S and SO_2 were produced in amounts much lower than expected from the reduction in total H_2S (H_2S + H_2S_x) in the liquid sulfur. Consequently, we propose that oxidation of H_2S and/or H_2S_x to elemental sulfur contributes to the overall removal of H_2S and H_2S_x during air sparging. Air sparging likely promotes the following reactions although it is not known to what extent each process occurs or whether some reactions are limited to the liquid sulfur phase or the headspace above the liquid sulfur:

$$H_2S_x + 1/2\ O_2 \rightarrow H_2O + \frac{x}{8} S_8 \qquad ...(2)$$

$$H_2S_x + 3/2O_2 \rightarrow H_2O + SO_2 + S_{x-1} \qquad ...(3) \qquad (x=1,2,3,...)$$

$$2\ H_2S + SO_2 \rightarrow 2\ H_2O + 3/8\ S_8 \qquad ...(4)$$

Use of morpholine or quinoline catalysts in combination with nitrogen sparging resulted in rapid removal of H_2S_x (Table 1). Only H_2S was observed in the headspace gases. The polymeric sulfur content (i.e. CS_2 insoluble sulfur) of sulfur solidified immediately after degassing to 10 ppmw residual total H_2S was zero when using morpholine as a degassing catalyst and ca. 4 weight % when using air. This result may be explained by an acid/base reaction of the amine with H_2S_x and intramolecular reaction of the resultant HS_x^- anion, every 8 sulfur atoms forming S_8 and, eventually, liberating H_2S.

$$R_1R_2NH + H_2S_x \rightarrow R_1R_2NH_2^+HS_x^-$$

$$HS_x^- \rightarrow S_8 + HS_{x-8}^- \rightarrow S_8 + HS_{x-16}^- \rightarrow R_1R_2NH_2^+HS^- \rightarrow H_2S + R_1R_2NH$$

(where R_1R_2NH represents morpholine or any other reasonably basic amine)

Compression tests with sulfur obtained from air and amine catalyst degassed sulfur have revealed that the strength of the sulfur is dependent on the amount of polymeric sulfur in the sample. A 102 mm x 51 mm cylindrical pellet containing no polymeric sulfur withstood ca. 500 psi whereas a similar pellet containing 4 weight % polymeric sulfur withstood ca. 2000 psi before crumbling.

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