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Solubility of Elemental Sulfur in Toluene between (267.15 and 313.15) K under Atmospheric Pressure

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The occurrence of sulfur deposits in natural gas transmission facilities has recently been observed. Only modeling approaches of this subject are available and suggest desublimation of sulfur as the mechanism responsible for the deposit. Quantification of the sulfur deposit is the first step to an experimental study of the phenomenon. The solid present on polluted pieces is recovered by solving it in a toluene bath. Thus, experimental data concerning sulfur solubility in toluene are necessary for the deposit quantification. The analytical method developed in this work is based on the chemical reaction between elemental sulfur and triphenylphosphine to produce triphenylphosphine sulfide. Gas chromatography (GC) coupled with a flame photometric detector (FPD) in phosphorus mode allows sulfur quantification indirectly. This analysis method is used for determining the solubility of sulfur in toluene under atmospheric pressure and temperature ranging from (267.15 to 313.15) K.

Introduction

Deposition of sulfur during sour gas well exploitation has been a problem for the past several decades. Hyne[1] showed the difficulty in establishing a yardstick to explain sulfur deposition. Occurrence of sulfur deposits in natural gas transmission facilities has recently been observed. Pack[2] studied natural gas transportation and listed the most common places for its occurrences. It appears that the most common location is immediately downstream of a pressure reduction facility. One of the hypotheses proposed to explain the solid accumulation, based on a thermodynamic approach,[3] is the desublimation of sulfur. Indeed, during gas expansion, both the pressure and the temperature decrease. Consequently, the gas may become oversaturated in sulfur. Because it is below the sulfur triple point temperature (368.65 K[4]), part of the gaseous sulfur can be transformed into solid particles. This deposition can have serious consequences for pipeline operators. For instance, sulfur deposits can be observed around pressure control valves and then affect the stem movement or plug the valve orifice. Solid sulfur can also modify the accuracy of flow meters; Chesnoy and Pack[5] reported that the deposit could introduce a measurement error of up to 2 % and in some cases even more. In our laboratory, to quantify the sulfur deposit, each piece on which the deposit is formed is immersed in a toluene bath. Several excellent solvents for sulfur are well-known,[4,6] like carbon disulfide, carbon tetrachloride, or benzene. Nevertheless, in our specific case, the solvent should be effective but as nontoxic as possible and easy to handle. That is why toluene was chosen. To propose and optimize our cleaning process, experimental data of sulfur solubility in toluene are necessary. Available studies on this subject are old and very sparse: Seidell[7] reported the results of different works done in the 20s and is cited by Tuller.[4] Moreover, the experimental protocol used is not described in these studies.

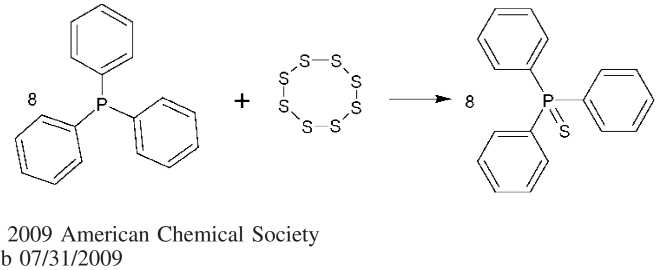
Several methods, referenced by Lesage and Clark,[8] can be used to analyze sulfur. Some methods employ oxido-reduction reactions with quantification of sulfates or sulfides by spectrophotometric, polargraphic, or volumetric titration. Other methods more difficult to reproduce use extraction, gravity, or colorimetry. The last methods are direct analyses based on chromatography (GC or HPLC).

In this work, the solubility of sulfur in toluene was experimentally obtained in two steps. The first step consists of saturating toluene in sulfur. During the second step, sulfur reacts with triphenylphosphine (TPP) to form sulfur triphenylphosphine (TPPS). The TPPS concentration is obtained by GC, and then, the sulfur saturation value is indirectly quantified. This work aims to provide experimental data of sulfur solubility in toluene under atmospheric pressure and temperature ranging from (267.15 to 313.15) K.

Experimental Section

Materials. Chemicals. Sulfur was a high-purity finely dispersed solid distributed by Merck with a content of (99.0 to 100.0) %. Triphenylphosphine (TPP), triphenylphosphine sulfide (TPPS), and triphenylphosphate ($TPPO_4$) were Merck's products for synthesis and are each 99 % pure. Toluene (purity

Scheme 1. Chemical Reaction between Triphenylphosphine (TPP) and Elementary Sulfur (S_8)



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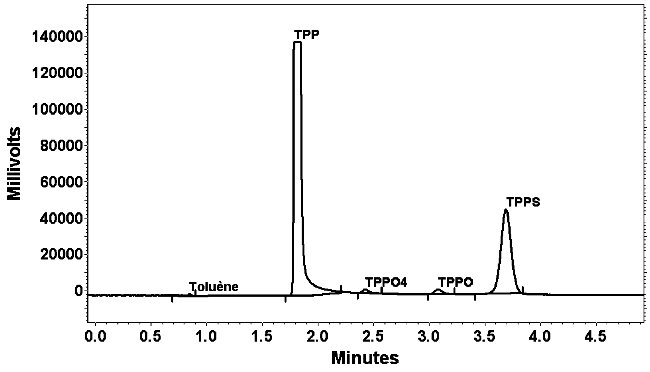

Figure 1. Typical chromatograph for the analysis of S_8 using TPP.

$>$ 99.8 %) was obtained from Fisher Bioblock Scientific. Ethanol (purity > 99.5 %) was obtained from Merck.

Gases used for chromatography were supplied by Air Liquide. Helium had a stated purity of more than 99.999 %, and hydrogen was 99.995 % pure. A mixture of 80 % of nitrogen and 20 % of oxygen was used to ignite the flame of the chromatograph detector.

Gas Chromatograph. Samples were analyzed on a ThermoFisher Scientific Trace GC Ultra gas chromatograph coupled with a flame photometric detector (FPD), which is specific for sulfur and phosphorus. Because TPPS contains a phosphorus atom, the FPD is used in phosphorus mode with a 560 nm interference filter and a base at 593.15 K. Helium was used as carrier gas at a column flow rate of $8.33 \cdot 10^{-2}$ $cm^3 \cdot s^{-1}$, and the Split/Splitless Injector was operated at 573.15 K with a split ratio of 10. A TR-5 Trace GC Capillary Column (0.53 mm id, 1 μm thickness, and 30 m length) was used in isotherm mode at 563.15 K.

Protocol/Method. Saturating the Solution. The experimental device consisted of a cylindrical glass vessel enclosed by its double envelope. The volume of the glass stirred reactor is 0.3 dm^3. The thermostatted bath, coupled to the double envelope, permitted us to maintain a constant temperature (± 0.05 K). The heat transfer fluid was a monopropylene glycol-demineralized water mixture. Pressure was fixed to the atmospheric pressure. First, 12 g of solid sulfur is introduced in the reactor. Next, the solvent is added. To help the solubilization of sulfur in toluene, the solution is mixed thanks to a magnetic stirring, and the temperature was set 10 °C higher than the temperature of the experiment. For instance, when we determined the solubility of the sulfur at 313.15 K, the temperature was initially set to 323.15 K. Then, the temperature was gradually decreased to the temperature of the experiment. The solution was stirred for 12 h at fixed temperature. A study of the evolution of the concentration over time ensured that stirring during a half-day is sufficient to reach equilibrium.

Table 1. Mass Fraction (w) Solubility of Sulfur in Toluene from T = (267.15 to 313) K

T/K	100 w
312.95	2.800 ± 0.097
303.35	2.121 ± 0.080
293.25	1.695 ± 0.049
284.15	1.266 ± 0.014
274.95	1.042 ± 0.009
267.15	0.782 ± 0.023

Analysis. Once the toluene was saturated with sulfur, the stirring was stopped. Thirty minutes later, the time necessary for settling of the fine particles of solid sulfur present in the solution, 1 cm^3 of this solution was sampled, weighed, and diluted. TPP and $TPPO_4$ were added in the last dilution at concentrations determined in the next section. 10^{-3} cm^3 of the final solution was injected in the chromatograph. To ensure maximum cleanliness of the syringe, it was flushed at least 60 times with toluene and ethanol. Pure toluene was injected to verify the cleanliness of the syringe. For each temperature, three experiments were conducted, and each injection sample was repeated 5 times.

Principle of the Gas Chromatography Analysis. The chemical reaction developed by Bartlett and Mergurian[9] is the basis of the analytical method used in this paper. This reaction between elemental sulfur and triphenylphosphine (TPP) leads to the formation of sulfur triphenylphosphine (TPPS), according to the reaction scheme given on Scheme 1.

A sample of the sulfur saturated solution is added to a solution with an excess of TPP. Sulfur contained in this sample comes into contact with TPP and reacts completely to form triphenylphosphine sulfide (TPPS). The product of the reaction (TPPS) is volatile and thermally stable enough to be quantified using gas chromatography. The analytical method developed by Lesage and Clark[8] and Davis et al.[10] is used. With an internal

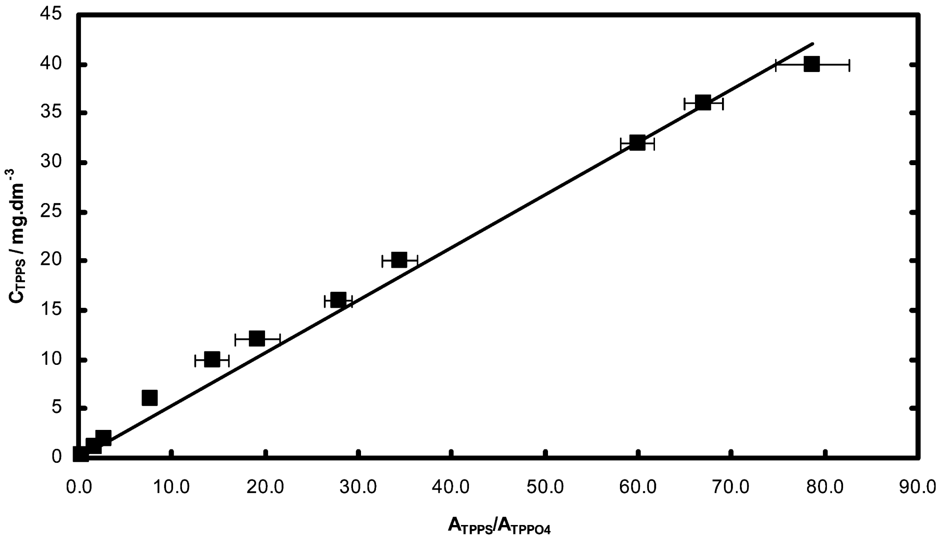

Figure 2. Calibration line for quantification of triphenylphosphine sulfide (TPPS). ■, experimental ratio of areas peak of TPP and $TPPO_4$ depending on the concentration of TPPS; and −, trend line of calibration.

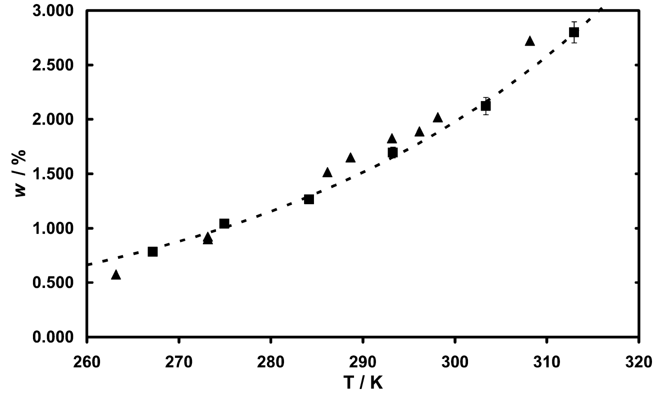

Figure 3. Mass fraction (*w*) solubility of sulfur in toluene. ■, this work; ▲, ref 5; - -, empirical correlation.

calibration of the trapping mixture, the concentration is determined with precision. Concentration of internal standard $TPPO_4$ is fixed at 1.5 $mg \cdot dm^{-3}$. A typical chromatogram produced from the analysis of a sample is presented in Figure 1. The four peaks generated by this analysis represent the unreacted TPP introduced in excess in the trapping solution, the internal standard $TPPO_4$ with a known concentration, the triphenyloxide (TPPO) formed by oxidation of TPP, and the product of the reaction TPPS.

Toluene is chosen as solvent of the reaction. This choice has the advantage of being the same as the one chosen in our laboratory to clean pieces affected by sulfur deposits. In addition, Clark and Lesage[8] indicated that toluene was a good solvent for this reaction. According to the reaction scheme given in Scheme 1, stoichiometric conditions require a quantity of TPP 8 times higher than the quantity of sulfur. Nevertheless, to significantly increase the efficiency of the reaction, it is necessary to introduce a large excess of TPP, so a concentration of 200 $mg \cdot dm^{-3}$ was chosen.

Concerning the internal standard, a solution concentrated to 150 $mg \cdot dm^{-3}$ of $TPPO_4$ was first prepared by measuring a mass of 0.15 g (± 0.1 mg precision) and adding the adjusted volume of toluene in a 1 L volumetric flask. One cm^3 of this solution is mixed with the sample of sulfur saturated solution and the excess of TPP.

The consequence of this large excess of TPP is that the pick of TPP is saturated on the chromatograms. This also ensured us that enough TPP has been added in the final solution and that the parallel reaction, oxidation of TPP, does not perturb the main reaction. As mentioned by Clark and Lesage,[8] contact of the samples with air should be minimized, and because the kinetic of this parallel reaction is slow it does not interfere with analyses carried out over reasonable time periods. Indeed, there is no interference of the TPPO's pick while its content is sufficiently low.

To obtain the calibration line, several solutions of TPPS at different concentrations are prepared by measuring the weight of each product and the volume of solvent and successive dilutions. The concentration of internal standard $TPPO_4$ is fixed at 1.5 $mg \cdot dm^{-3}$. The ratio area of the pick of TPPS on the peak area of $TPPO_4$ depends on the TPPS concentration. The corresponding calibration curve is presented in Figure 2. The linear equation allows the quantification of the TPPS contained in a trapping solution of unknown concentration.

For each experiment on a given amount of TPPS, we calculate the relative standard deviation RDS given by

$$\mathrm{RDS} = \frac{\sigma_X}{\bar{X}} \qquad (1)$$

$$\sigma_X^2 = \frac{1}{n}\sum_{i=1}^{n}(X_i - \bar{X}) \qquad (2)$$

$$\bar{X} = \frac{1}{n}\sum_{i=1}^{n}X_i \qquad (3)$$

where σ_X is the standard deviation, and $\bar{X}$ is the average of n values of X_i ($i = 1 \ldots n$).

For all the experiments, the RDS is 4.2 %, and error bars for each experiment are indicated in Figure 2.

This method of analysis by gas chromatography has the following range of quantification: 0.2 $mg \cdot dm^{-3} < C_{TPPS} < 40$ $mg \cdot dm^{-3}$. The minimum detectable level for the flame photometric detector is 0.1 $pg \cdot s^{-1}$. With a concentration below the lower limit, the signal received by chromatographic analysis is not reproducible. With a concentration above the upper limit, the signal is cut. As the concentration of TPPS is directly related to sulfur, it is necessary to dilute high-concentrated samples before analysis.

Results and Discussion

Validation of Analytical Method. Before experiments, it is necessary to validate the analytical method of sulfur quantification. Samples of known concentration in sulfur are prepared. A mass of solid sulfur is weighed accurately with a precision of 0.1 mg, and nonsaturated solutions are obtained by successive dilutions. TPP and $TPPO_4$ are introduced in the last diluted solution, and this one is injected in the chromatograph. The quantity of sulfur contained in the solution is indirectly determined from the GC analysis results, and this quantity is compared with the known value. For instance, we prepared a solution containing 9.23 $mg \cdot dm^{-3}$ of TPPS. The average concentration of TPPS obtained with different injection of samples is (9.16 ± 0.37) $mg \cdot dm^{-3}$. A deviation of 0.7 % between the theoretical weighted value and the value obtained by chromatographic analysis demonstrates the accuracy of the chromatographic method used.

Solubility of Sulfur in Toluene. In this work, solubility of sulfur in toluene is studied at seven different temperatures. Thus, this solubility is studied between (267.15 and 313.15) K. Experimental data are collected in Table 1. Figure 3 shows the comparison between our results and those compiled by Tuller[4] in 1940.

Our experimental results show that the solubility of sulfur in toluene increases with temperature. Each injection is repeated 5 times to ensure the very good reproducibility of our measures.

Standard deviation is given in Table 1. The relative standard deviation consistently below 4 % is found for each analysis.

Between (267.15 and 275.15) K, our experimental results match accurately the values available. Nevertheless, a slight deviation between our results and those of the literature is observed above 275.15 K. Indeed, values reported by Tuller[4] are greater than our data. An empirical correlation was fitted from the experimental results of this work

$$100\,w = -5.845 + 8.52 \cdot 10^{-2}\exp\left(\frac{T/\mathrm{K}}{39.2766}\right) \qquad (4)$$

Conclusions

Deposition of elemental sulfur in natural gas transmission line systems is a serious problem in the transport network.

Quantification of solid sulfur is a necessary step to study the phenomenon. An analytical method of quantification of sulfur is developed. It consists of a chemical reaction between elementary sulfur and triphenylphosphine to produce triphenylphosphine sulfide. Toluene is chosen as solvent. Gas chromatography analysis coupled with a flame photometric detector allows TPPS quantification. After validating the method by analysis of a solution with a known concentration of sulfur, it is used for determining experimentally the solubility of sulfur in toluene under atmospheric pressure and temperature ranging from (267.15 to 313.15) K.

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