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Experimental Studies of Solubility of Elemental Sulfur in Methane at 363.15 K for Pressure Ranging from (4 to 25) MPa

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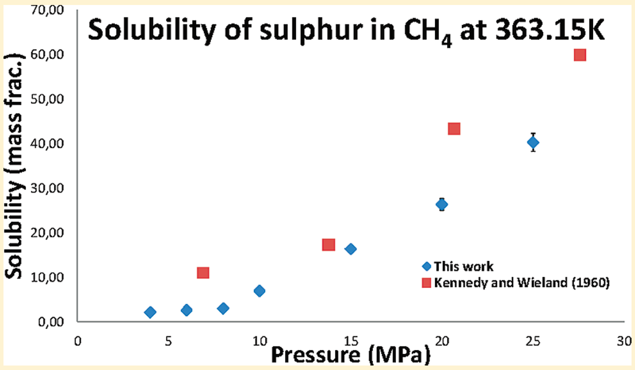
ABSTRACT: In recent years, many problems of elemental sulfur deposits in natural gas transmission line systems have been noted. These problems occur very often immediately downstream of a pressure reduction facility. To prevent the apparition of solid sulfur deposits causing security and maintenance problems it is imperative to determine sulfur solubility in natural gas at pressures and temperatures corresponding to transport conditions. In a previous work (Serin et al. *J. Supercrit. Fluids* **2010**, *53*, 12−16), an original experimental apparatus was designed, and experimental saturation values of carbon dioxide in sulfur were obtained. The protocol principle is schematically divided into three steps: saturation, trapping, and quantification. In this work, experimental sulfur solubility in methane was measured and compared to available studies at 363.15 K in the pressure range from (4 to 25) MPa. This paper presents these measurements and the improvements of the trapping and quantification steps that have been made to get these solubility data.



1. INTRODUCTION

In gas transport networks, the natural gas pressure ranges usually from (2 to 8) MPa. Since the operational pressure of gas distribution networks is around 0.5 MPa, gas expansion facilities are used to depressurize the gas. For several years now, the occurrence of solid deposits has been reported in these networks and in particular just behind the gas expander.[1−3] The LaTEP (Laboratoire de Thermique Energétique et Procédés) has been working on sulfur deposition issues for about 10 years. To protect the gas network from the appearance of solid sulfur, which causes security problems and additional operating costs, it is imperative to determine the solubility of sulfur in natural gas. A bibliographic study done by Serin et al.[4] showed that very few experimental data on the solubility of sulfur in natural gas are available in the literature.[5−8] An original experimental apparatus for measuring the sulfur solubility in gases was developed by the same authors.[4] They measured sulfur solubility in carbon dioxide at (333.15 and 363.15) K with pressures ranging from (10 to 30) MPa.

The aim of the present study is to determine the solubility of sulfur in methane, which is a major component of natural gases at 363.15 K in the pressure range of (4 to 25) MPa. To do so, the experimental facility used in ref 4 was improved.

2. EXPERIMENTAL SECTION

a. General Overview. A detailed description of the experimental pilot is available in Serin et al.[4] The principle of the experimental pilot can be summarized in three steps: saturation of the gas with sulfur, trapping of all dissolved gaseous sulfur and finally quantification. The improvements made concern the last two steps.

b. Material and Protocol Improvements. *Materials.* Sulfur is 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$_4$) are Merck's products for synthesis and are 99 % pure each. Toluene (purity >99.8 %) is obtained from Fisher Bioblock Scientific and Ethanol (purity >99.5 %) from

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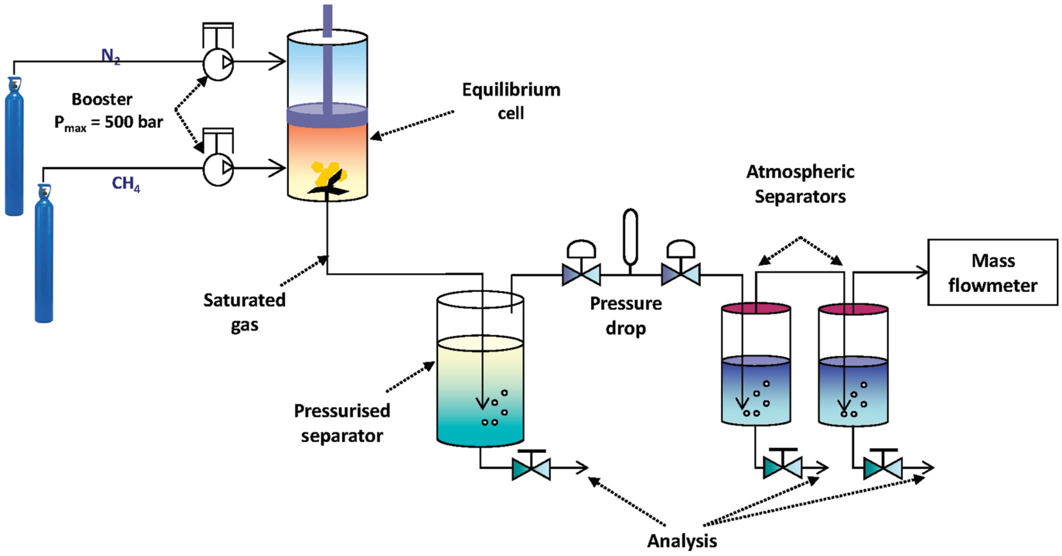

Figure 1. Experimental facility diagram.

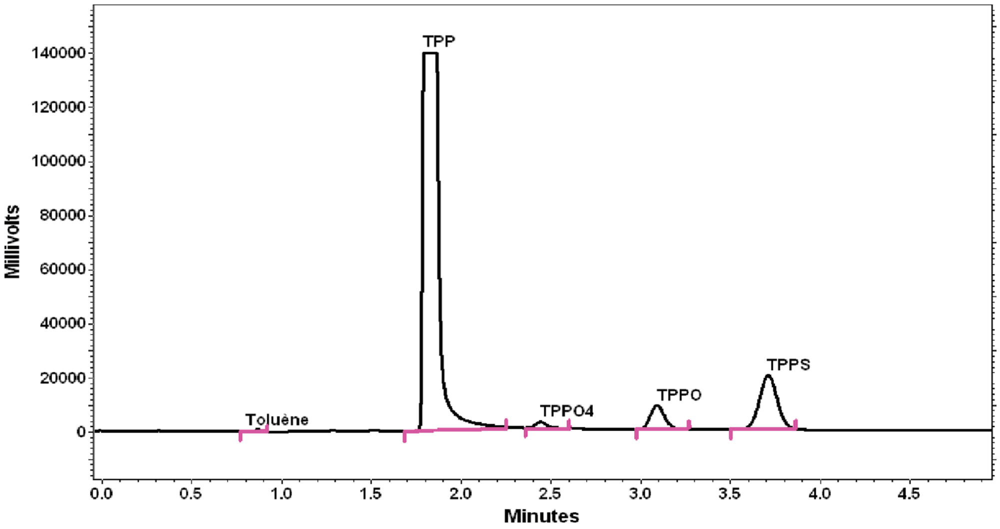

Figure 2. Example of chromatogram.

Merck. Gases used are supplied by Air Liquide. For the saturation pilot, the nitrogen is an industrial gas, and the methane is 99 % pure. For the chromatography, the helium has a stated purity of 99.999 %, and the hydrogen is 99.995 % pure. A mixture of 80 % of nitrogen and 20 % of oxygen is used to ignite the flame of the chromatograph detector.

Gas chromatography samples were analyzed on a Thermo-Fisher Scientific Trace GC UltraTM gas chromatograph coupled with a flame photometric detector (FPD), which is specific for sulfur and phosphorus. Because TPPS contains a phosphorus atom, the FPD was used in phosphorus mode with a 560 nm interference filter and a base at 593.15 K.

Saturation Step. As written before, no modification was done for this step. The same equilibrium cell is used to provide gas saturation.[4]

Improvement of the Trapping Step. The saturated gas, evacuated from the equilibrium cell, was previously expanded close to atmospheric pressure thanks to a valve. Then, the gas was bubbled into a trapping mixture placed in two stainless steel bottles at atmospheric pressure. During the gas expansion through the valve a part of the gaseous sulfur became solid. Then, to recover all the sulfur, the filters placed after the valve had to be rinsed with another trapping solution. After that, the trapping solutions and the rinsing solution had to be analyzed.[4]

The first modification consists in trapping a part of the gaseous sulfur under the working pressure and not under the atmospheric pressure. For that a new separator (named the pressurized separator on Figure 1) is added. It has a capacity of 1.2 L, and its maximum operating conditions are 500 K and 50 MPa. The following two separators operate at atmospheric pressure. They have a capacity of 2.5 L, and their maximum operating conditions are 373.15 K and 1 MPa. Thus, a first trapping takes place under pressure, and a second sulfur trapping occurs in the other separators. The last separator is used to ensure that all the sulfur present in the gas has been trapped.

The second modification concerns the gas expansion process. It is now provided by a system of two pneumatic valves and a capacity of 5 mL. The first valve located upstream of the capacity opens, the gas fills the capacity, and the valve closes. Then the second valve located downstream of the capacity

Table 1. Sulfur Solubility Table[a]

set of data	T K	P MPa	w_s mass fraction	RSD %
this work	363.2	4	$2.97\cdot10^{-6}$	5
		6	$3.60\cdot10^{-6}$	5
		8	$4.21\cdot10^{-6}$	5
		10	$9.75\cdot10^{-6}$	5
		15	$2.30\cdot10^{-5}$	5
		20	$3.71\cdot10^{-5}$	5
		25	$5.68\cdot10^{-5}$	5
Kennedy and Wieland (1960)	366.5	6.9	$1.55\cdot10^{-5}$	
		13.8	$2.43\cdot10^{-5}$	
		20.4	$6.11\cdot10^{-5}$	
		27.6	$8.45\cdot10^{-5}$	

[a] For this work the uncertainty on temperature is 0.1 K, and the uncertainty on pressure is 0.01 MPa.

opens and the gas flows out of the capacity. This operation is repeated as many times as needed to drain the equilibrium cell. This system can expand the gas in a controlled and secure way, down to a pressure close to ambient.

The main advantages of these two modifications are the nonappearance of solid sulfur in all of the tubing and an accurate control of the flow of the evacuated gas. Indeed, solid accumulation in the filters could create variations in the flow during gas evacuation, which could compromise the experiment. Consequently, there is now no need to rinse the tubing, and the pressure discharge process is secured.

Improvement of the Analysis Steps. The analytical method developed by Lesage and Clark[9] and Davis et al.[10] is used. The concentration of internal standard $TPPO_4$, fixed at 3 $mg\cdot L^{-1}$, allows an accurate determination of the TPPS amount. The details of this analytical method are presented in Jay et al.[11]

An auto sampler is used. It contributes to a better reproducibility of the injections and allows programming of multiple fully automated analysis methods. Since the products are adsorbed on the walls of the syringe, it is necessary to rinse it between two injections. Nearly 60 rinses with toluene and ethanol are needed to remove the excess of product in the syringe.[11] The automatic programming of these rinses allows on one hand avoiding a tedious task to the operator and on the other hand gaining a significant time because the 100 rinses are performed while a sample is analyzed.

A typical chromatogram is displayed on Figure 2. The elution order does not change. The first observed peak corresponds to the solvent injection. It is followed by the peaks of the products in the analyzed sample. The saturated peak of TPP indicates that all of the reactant did not disappear, so that the excess of TPP was sufficient. It is also observed in addition to the internal standard ($TPPO_4$) and reaction product (TPPS) peaks the occurrence of one last peak: triphenylphosphine oxide (TPPO). Its presence is due to the product of the oxidation reaction of TPP with ambient oxygen.

The integration of the peak area of the chromatogram allows us to determine the mass concentration of TPPS in the sample. Thus we can obtain the mass of sulfur trapped in the solution and deduce the solubility of sulfur in the gas.

3. EXPERIMENTAL RESULTS AND DISCUSSION

a. CPG Calibration. Before we began the experimentations a calibration was achieved. Eleven solutions with a constant concentration in $TPPO_4$ (3 $mg\cdot L^{-1}$) and TPPS concentrations ranging from (2 to 40) $mg\cdot L^{-1}$ were analyzed. Each of these solutions was analyzed five times. An analysis of variances was performed on the results of this calibration. This analysis

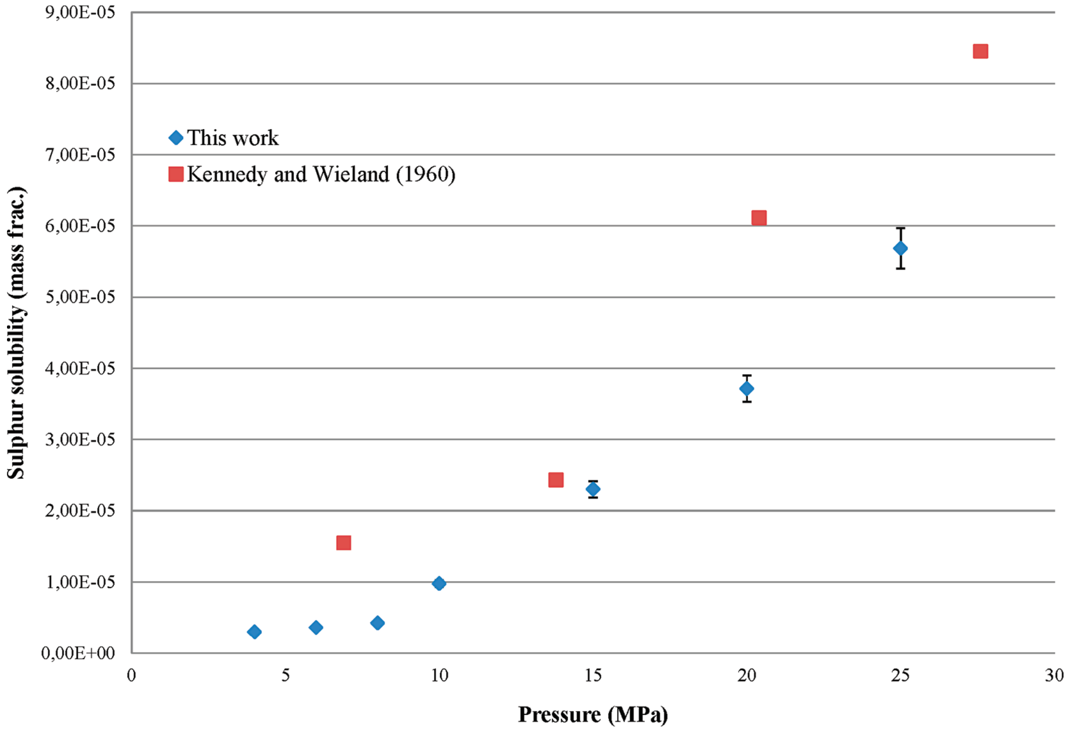

Figure 3. Solubility of sulfur in CH_4 at 363.15 K.

allowed us to calculate a relative standard deviation (RSD) equal to 0.55 %

$$\mathrm{RSD} = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n - 1}} \qquad (1)$$

b. CH_4 Isotherm. Experimental measurements of sulfur solubility in methane at 363.15 K in the pressure range of (10 to 25) MPa have been performed with the apparatus presented above. Experimental saturation values of sulfur in methane are not numerous. Only Kennedy and Wieland[6] provided this kind of measurements for the conditions of temperature and pressure studied in this work. These solubility data are given in Table 1 and Figure 3. The relative standard deviation is equal to 5 %.

Our solubility values range from (10 to 25) MPa. At constant temperature, the sulfur solubility increases with pressure, but our results show a lower influence of pressure compared to Kennedy and Wieland.[6] The comparison between the solubility isotherm of sulfur at 363.15 K in the pressure range of (10 to 30) MPa in carbon dioxide[1] and in methane (this work) indicates that the values are greater in carbon dioxide. Moreover, the higher the pressure, the greater the difference is. For instance, at 15 MPa, sulfur solubility is about 3 times greater in carbon dioxide than in methane, while it is about 5 times at 30 MPa.

4. CONCLUSIONS

To understand the behavior of sulfur in natural gas and particularly its deposition, experimental data are needed. For that, in a previous work,[1] an original experimental pilot was presented and used to perform sulfur solubility measurements in carbon dioxide.

In this work we presented experimental solubility values of sulfur in methane, the major component of natural gases, at 363.15 K in a pressure range of (4 to 25) MPa. This solubility isotherm is compared to the only study available.[6] The solubility values range from $2.97 \cdot 10^{-6}$ to $5.68 \cdot 10^{-5}$ in mass fraction. The values at the lowest pressures correspond to the natural gas transportation conditions and are the first measurements made in these conditions. Our results are slightly different from those obtained by Kennedy and Wieland.[6] Indeed, our solubility data are lower and show a lower influence of pressure.

To obtain these experimental data improvements have been made to the experimental device. Two of the three steps of the protocol have been improved. The gaseous sulfur is now partially trapped under pressure and before the gas is expanded. The gas expansion system and the analysis method have also been modified to gain accuracy, security, and time.

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Notes

The authors declare no competing financial interest.

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