# Measurement and Modeling of the Solubility of Tetramethylthiuram Disulfide and 2-Nitrophenyl Disulfide in Compressed Propane

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ABSTRACT: The solubility of tetramethylthiuram disulfide (TTDS) and 2-nitrophenyl disulfide (NPDS) in sub- and supercritical propane has been experimentally determined in a static view cell, for temperatures between (347 and 393) K and pressures in the range (4.8 to 12.9) MPa. The solubilities of TTDS varied from (0.09 to 0.67) mg of solute per gram of propane, whereas those of NPDS were from (0.06 to 0.70) mg of solute per gram of propane within the experimental range studied. It was found that larger values of the solubility were obtained at higher pressures. Regarding the temperature effect, for NPDS the solubility rose with increasing values of the variable in the whole experimental range analyzed, while for TTDS higher solubilities were found at 370 K (the critical temperature of propane). The solubility values obtained for these compounds were compared to those of anthracene, carbazole, and dibenzothiophene (DBT) in propane. It was observed that TTDS and NPDS solubilities are similar to those of carbazole and 1 or 2 orders of magnitude smaller than those of anthracene or DBT. These results have been explained taking into account the solute's vapor pressure and the polarity of both the solvent and the solutes. With this purpose, dipole moments of all solutes compared were calculated using the HyperChem computational chemistry package. TTDS and NPDS solubility in propane was modeled by the Peng−Robinson equation of state. Using a set of mixing rules with two parameters a good fitting of the experimental results was attained. Physical properties of TTDS and NPDS required for solubility modeling by the Peng−Robinson equation were calculated using estimation methods previously proposed in the literature.
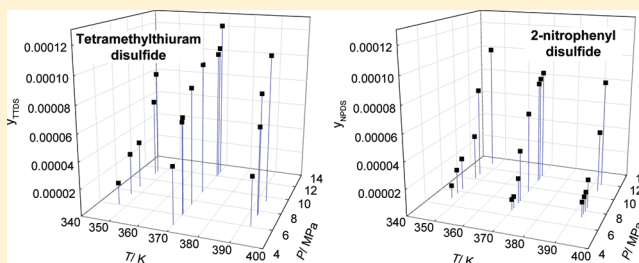
1. INTRODUCTION

Tetramethylthiuram disulfide (TTDS, commonly known as thiram) and 2-nitrophenyl disulfide (NPDS) are two examples of disulfide nitrogen organic (hydrocarbon and polyaromatic) compounds. These types of compounds are often used in the formulation of different industrial products, such as fungicides, insecticides, bacteriostatics, seed disinfectants, detergents, as well as accelerator additives in rubber vulcanization processes.[1] They are toxic and/or mutagenic, and due to their low biodegradability, they persist in soils and sediments for several months, so they can be transferred also to water reservoirs.[2,3]

In this context, physical-chemical methods seem to be the effective solution to degrade or remove these pollutants from the contaminated media. Several works in the literature discuss the degradation of TTDS and other common pesticides in aqueous solution by chemical oxidation,[4−6] using ozone and ultraviolet radiation,[7] and by TiO$_2$ photocatalytic degradation.[8,9] Moreover, for some specific situations, such as highly polluted but relatively narrow spots (e.g., local spilled persistent organic pollutants), supercritical fluid extraction (a physical-chemical treatment) has been shown to be a good choice to be used as remediation technology.[10−12]

Concerning the supercritical fluid extraction technology, a common factor considered important for the application of supercritical fluid extraction technology is the need of a thorough understanding and knowledge of the target solute's solubility in the supercritical fluid to be used as solvent. Together with the mass transfer coefficients, they are required to design the operation units or to develop first approach models of the extraction processes.

Taking all of this into account, in this work the solubilities of TTDS and NPDS as models of disulfide nitrogen organic compounds have been measured in compressed propane. In earlier works the solubilities of anthracene, carbazole, and dibenzothiophene (DBT) using propane as solvent were reported.[13−15] Propane has been the solvent of choice because it has been recently demonstrated that it presents better solvent properties than CO$_2$ for high molecular weight aromatic hydrocarbons.

In this paper, TTDS and NPDS solubilities in sub- and supercritical propane have been experimentally determined between (347 and 393) K in a pressure range from (4.8 to 12.9) MPa. The solubility data obtained have been modeled by the Peng−Robinson equation of state.[16] For this purpose, different physical properties (such as critical pressure and temperature, acentric factor, and vapor pressure) of the solutes (TTDS and NPDS) are required, and due to their lack in the scientific
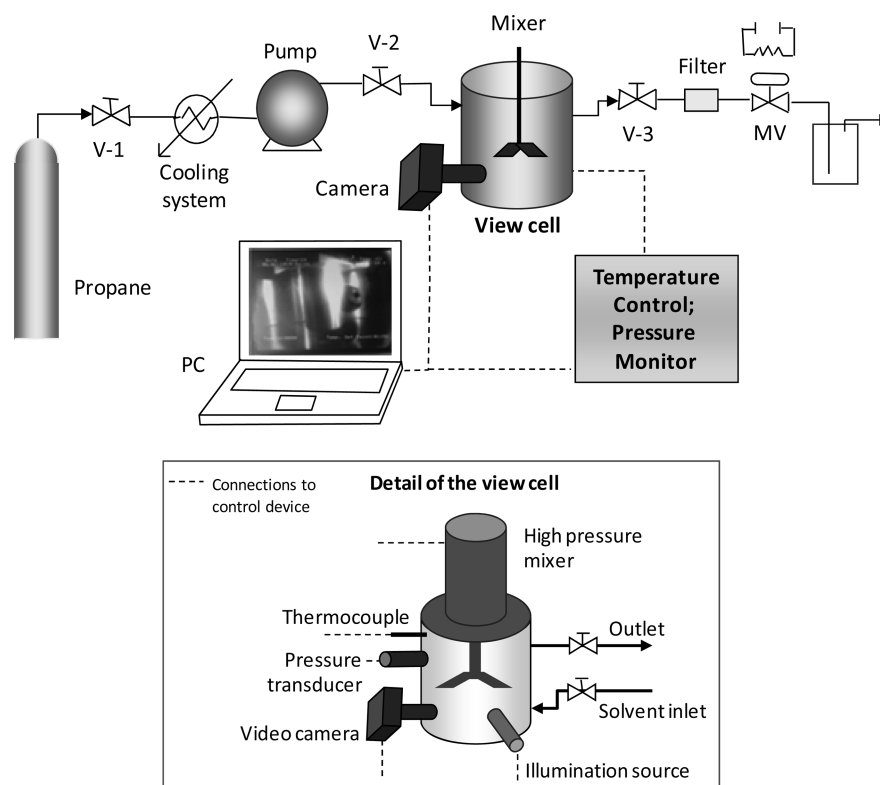
Figure 1. Layout of the experimental setup.

literature, they have been estimated using different methods available in bibliography, such as the Wilson and Jasperson method for critical constants, the Pitzer expansion equation for acentric factors, and the Ambrose–Walton corresponding states method for vapor pressures.[17-21]

2. EXPERIMENTAL SECTION

2.1. Materials and Experimental Setup. The solubility of the solutes (TTDS and NPDS) in propane has been measured in an experimental setup (R100CW) supplied by Thar Technology, Inc. (Pittsburgh, PA). It is schematically shown in Figure 1 and consists of a cylindrical view cell (volume 0.1 L) with two sapphire windows mounted 90° apart for the observation and recording of the phase behavior inside the cell using a camera and an illumination source. It is equipped with a pressure transducer, a temperature controller (with embedded heaters), a high pressure motor-driven mixer, and a pressure pump (P-50, Thar Technology). A cooling system was used to cool the propane before it was pumped to the solubility determination equipment. The camera, which was connected to a personal computer (PC), allowed the observation and recording of the phase behavior inside the cell under all of the pressure and temperature conditions tested. For decompressing the system, a metering valve (MV) with a heating device was used. A filter protected the metering valve against potential blockage due to solidification of the solutes during decompression. Pressure and temperature can be measured with an accuracy of 0.01 MPa and 0.1 K, respectively, but the control system of the equipment allows pressure and temperature variations in the cell in the ranges ± 0.2 MPa and ± 3 °C, respectively. These pressure and temperature variations (± 0.2 MPa and ± 3 °C) were considered to evaluate the uncertainties in

propane density, propane mass, and solute mole fraction, as indicated below.

The amount of solute (TTDS and NPDS) used in the experiments was weighed in an ED224S balance supplied by Sartorius (Germany), whose accuracy is 0.1 mg.

Propane (mass fraction 0.995, Praxair), tetramethylthiuram disulfide (mass fraction 0.970, Aldrich), and 2-nitrophenyl disulfide (mass fraction 0.990, Aldrich) were employed without further purification.

2.2. Experimental Procedure. To obtain the solubility data, a given amount of solute (TTDS and NPDS) was placed inside the cell. After that, the cell was closed and heated up to a given temperature by means of the embedded heaters and the temperature controller. Once the set temperature was reached, the mixer was switched on and the propane pumped into the cell. To determine the solute solubility, the pressure was increased (at isothermal conditions) in short intervals of (0.2 to 0.4) MPa until the point at which only one phase was observed through the sapphire window. Between intervals, the pressure was held for about 5 min before the next increase. The experiments were recorded in the PC connected to the camera. This allowed the subsequent viewing of the phase equilibrium images with their corresponding real-time pressure and temperature data. The solubility was determined from the amounts of solute (TTDS and NPDS) and propane loaded into the cell. The amount of propane in the cell was determined from the volume of the cell and the density of propane at the conditions of the test, according to $m_{propane} = \rho \cdot V$, in which ρ and V are the propane density and the cell volume, respectively. The volume occupied by the solute was not considered since it was extremely small compared to the cell volume. The propane mass uncertainty introduced by these approaches is indicated below.

The experimental pressure and temperature conditions used in each experiment are marked in Figure 2, where the regions
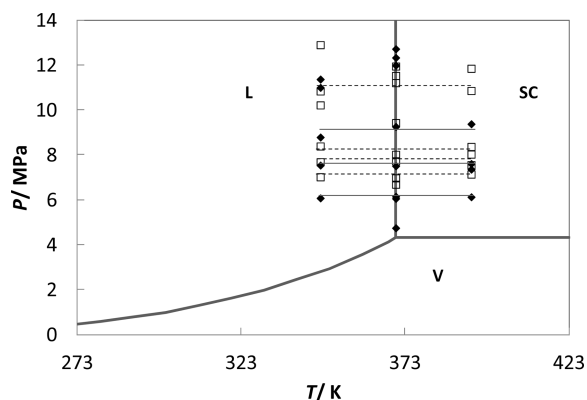

Figure 2. Experimental conditions marked in the phase diagram of propane, solute: ◆, TTDS; □, NPDS. Quasi-isobars: solid line, TTDS; dotted line, NPDS.

for liquid, vapor, and supercritical states of propane are also indicated. Solid and dotted lines are also drawn in Figure 2 to indicate the quasi-isobars at which the temperature effect was investigated for TTDS and NPDS, respectively.

Finally, it should be mentioned that, according to the manufacturer's specifications of the equipment, the standard uncertainty in the cell volume was 1 mL, and the possible pressure and temperature variations in the cell were in the ranges ± 0.2 MPa and ± 3 °C, respectively. On the other hand, the uncertainty associated with the propane density was 2.3 %, as estimated on the basis of three major influences: pressure and temperature effects on the density and the uncertainty in the reference data for the density (below 2 %).[22] According to the relationship between mass and density of propane (i.e., $m_{propane} = \rho \cdot V$, in which ρ and V are the propane density and the cell volume, respectively), the relative combined standard uncertainty in the propane mass, $u_r(m_{propane})$, was 0.025 [i.e., $u_r(m_{propane}) = \Delta m_{propane}/m_{propane} = 0.025$]. The uncertainty in the mass of solute was 0.5 mg, according to the balance calibration certificate and the manufacturer recommendations. The standard uncertainties in the molar masses[23] were (0.003) g·mol^{-1} for propane, (0.02) g·mol^{-1} for TTDS, and (0.02) g·mol^{-1} for NPDS.

Lastly, all of these uncertainty data and an error propagation analysis[24,25] allowed the uncertainty in the TTDS and NPDS mole fractions to be estimated. The results obtained are shown in Tables 1 and 2, respectively. It can be observed that, in all cases, the relative uncertainty in the mole fraction of TTDS, $u_r(y_{TTDS})$, is less than or equal to 0.13 [i.e., $u_r(y_{TTDS}) = \Delta y_{TTDS}/y_{TTDS} \leq 0.13$] and less than or equal to 0.24 for NPDS. These values were subsequently confirmed through repeatability tests.

3. ESTIMATION OF PROPERTIES OF TETRAMETHYLTHIURAM DISULFIDE AND 2-NITROPHENYL DISULFIDE

Physical properties of TTDS, NPDS, and propane are shown in Table 3. Data for critical constants, acentric factor, and vapor pressure of TTDS and NPDS have not been reported in the literature, and since they are required in the modeling of the solubility by Peng–Robinson equation of state, they have been estimated in this work.

Table 1. Experimental Results of Tetramethylthiuram Disulfide Solubility in Propane

T/K	P/MPa	y_{TTDS}[a]	uncertainty[b] $\Delta y_{TTDS} \cdot y_{TTDS}^{-1}$
347	6.1	$1.6 \cdot 10^{-5}$	0.13
	7.6	$3.2 \cdot 10^{-5}$	0.07
	8.8	$3.6 \cdot 10^{-5}$	0.06
	11.0	$6.1 \cdot 10^{-5}$	0.04
	11.4	$8.3 \cdot 10^{-5}$	0.04
370	4.8	$4.2 \cdot 10^{-5}$	0.07
	6.1	$6.8 \cdot 10^{-5}$	0.05
	6.2	$7.1 \cdot 10^{-5}$	0.04
	7.5	$8.7 \cdot 10^{-5}$	0.04
	9.3	$9.9 \cdot 10^{-5}$	0.03
	12.0	$1.0 \cdot 10^{-4}$	0.03
	12.3	$1.1 \cdot 10^{-4}$	0.03
	12.7	$1.2 \cdot 10^{-4}$	0.03
393	6.1	$3.6 \cdot 10^{-5}$	0.12
	7.4	$6.5 \cdot 10^{-5}$	0.05
	7.6	$8.7 \cdot 10^{-5}$	0.04
	9.4	$1.1 \cdot 10^{-4}$	0.03

[a]Mole fraction of tetramethylthiuram disulfide (TTDS) in propane.
[b]Relative combined standard uncertainty of TTDS mole fraction.

Table 2. Experimental Results of 2-Nitrophenyl Disulfide Solubility in Propane

T/K	P/MPa	y_{NPDS}[a]	uncertainty[b] $\Delta y_{NPDS} \cdot y_{NPDS}^{-1}$
347	7.0	$9.6 \cdot 10^{-6}$	0.18
	7.7	$1.9 \cdot 10^{-5}$	0.09
	8.4	$2.5 \cdot 10^{-5}$	0.07
	10.2	$3.5 \cdot 10^{-5}$	0.05
	10.9	$7.1 \cdot 10^{-5}$	0.03
	12.9	$1.0 \cdot 10^{-4}$	0.03
370	6.7	$8.1 \cdot 10^{-6}$	0.24
	7.0	$8.8 \cdot 10^{-6}$	0.22
	7.7	$1.9 \cdot 10^{-5}$	0.10
	8.0	$3.9 \cdot 10^{-5}$	0.05
	9.4	$6.2 \cdot 10^{-5}$	0.04
	11.2	$8.0 \cdot 10^{-5}$	0.03
	11.5	$8.3 \cdot 10^{-5}$	0.03
	12.0	$8.6 \cdot 10^{-5}$	0.03
393	7.2	$1.1 \cdot 10^{-5}$	0.22
	7.6	$1.3 \cdot 10^{-5}$	0.18
	8.0	$1.4 \cdot 10^{-5}$	0.16
	8.4	$2.2 \cdot 10^{-5}$	0.10
	10.9	$4.7 \cdot 10^{-5}$	0.05
	11.9	$8.3 \cdot 10^{-5}$	0.03

[a]Mole fraction of 2-nitrophenyl disulfide (NPDS) in propane.
[b]Relative combined standard uncertainty of NPDS mole fraction.

Different group contribution methods have been proposed in the literature for the prediction of critical constants of pure compounds.[17,31−36] These methods mainly consist of the calculation of the critical constants by means of equations that take into account the frequency of groups of atoms present in a given molecule. The different methods include a limited number of groups of atoms whose contributions to the critical constants in a given equation are assigned through the study of a large number of compounds. They provide the advantage of quick estimates without the need of substantial computational resources. However, on the other hand, their applicability is

Table 3. Molar Mass (M), Normal Boiling Temperature (T_{bp}), Melting Temperature (T_{mp}), Critical Temperature (T_c), Critical Pressure (P_c), and Acentric Factor (ω) of TTDS, NPDS, and Propane

	M	T_{bp}	T_{mp}	T_c	P_c	
compound	g·mol⁻¹	K	K	K	MPa	ω
propane	44.097[a]	231.06[b]	85.5[c]	369.825[d]	4.24733[b]	0.1518[e]
TTDS	240.44[a]	580.6[f]	429[f]			
NPDS	308.34[a]	715.0[f]	466[f]			

[a]Value taken from ref 23. [b]Value taken from ref 26. [c]Value taken from ref 27. [d]Value taken from ref 28. [e]Value taken from ref 29. [f]Value taken from ref 30.

limited because of the oversimplification of the molecular structure representation by means of group contributions.[35]

In this work, several group contribution methods have been tested to estimate the critical constants of the disulfide compounds studied (TTDS and NPDS).[32,34,35] Unfortunately, the contribution groups defined by these methods were insufficient to represent the molecular structure of these compounds, due to the uncommon groups of atoms present in the disulfide compounds studied. As an example, the Marrero−Pardillo method[34] uses a bond contribution method which provides 167 pairs of groups (bonds), that is, an important number of groups compared to other methods (41 contribution groups considered by Joback−Reid method,[32] for instance). In case of TTDS, the bond between carbon and sulfur atoms cannot be defined, as it does not match to any of the 167 groups proposed. In addition, bonds between sulfur or nitro groups with an aromatic carbon are not included within the bond groups considered by the estimation method.

In this context, Wilson and Jasperson[17] developed an estimation method based mostly on atom contributions, which has been previously employed in the prediction of critical constants of disulfide compounds.[37] Its main advantages are the simplicity and breadth of substances as it treats organics as well as inorganics. In addition, according to Poling et al.[21] the accuracy of this method is comparable to that of those group contribution methods mentioned previously.[32,34]

In this work, critical pressures (P_c) and temperatures (T_c) of TTDS and NPDS have been predicted by Wilson and Jasperson method,[17] by eqs 1 to 3. At the first order the method considers atomic contributions along with boiling point (T_b) and number of rings in the molecule (N_r), while group contributions are used at the second order to correct the critical constants obtained.[21]

$$T_c = T_b / \left[(0.048271 - 0.019846 \cdot N_r + \sum_k N_k \cdot (\Delta tck) + \sum_j M_j \cdot (\Delta tcj))^{0.2} \right] \quad (1)$$

$$P_c = 0.0186233 \cdot T_c / [-0.96601 + \exp(Y)] \quad (2)$$

$$Y = -0.00922295 - 0.0290403 \cdot N_r + 0.041$$
$$\cdot \left(\sum_k N_k \cdot (\Delta pck) + \sum_j M_j \cdot (\Delta pcj) \right) \quad (3)$$

In these equations N_k is the number of atoms of type k with first-order atomic contributions Δtck and Δpck, and M_j is the number of groups of type j with second-order group contributions Δtcj and Δpcj. P_c is in bars, and T_b and T_c are absolute temperatures. Table 4 shows the detailed atomic and group contributions of substance TTDS for the prediction of T_c and P_c by the Wilson and Jasperson method as an example.

Table 4. Atomic and Group Contributions Used in T_c and P_c Estimation of the TTDS by the Wilson and Jasperson Method[17,21]

atom k	N_k	Δtck	Δpck	$\sum_k N_k \cdot (\Delta tck)$	$\sum_k N_k \cdot (\Delta pck)$
C	6	0.008532	0.72983	0.142154	10.9828
H	12	0.002793	0.12660		
N	2	0.019181	0.44805		
S	4	0.007271	1.04713		

group j	M_j	Δtcj	Δpcj	$\sum_j M_j \cdot (\Delta tcj)$	$\sum_j M_j \cdot (\Delta pcj)$
−NH₂, >NH, >N−	2	−0.004	0.000	−0.008	0.000
−SH, −S−, −SS−	3	0.000	0.000		

Table 5 summarizes the values of T_c and P_c of TTDS and NPDS predicted by this method.

Table 5. Values Predicted for Critical Temperature (T_c) and Pressure (P_c), Acentric Factor (ω), and Vapor Pressure (P_v) of TTDS and NPDS at Experimentally Studied Temperatures

parameter	units	TTDS	NPDS
T_c	K	807.2	961.4
P_c	MPa	2.56	2.05
ω		0.54438	0.63983
P_v (347 K)	MPa	9.41·10⁻⁶	1.06·10⁻⁸
P_v (370 K)	MPa	4.58·10⁻⁵	9.71·10⁻⁸
P_v (393 K)	MPa	1.78·10⁻⁴	6.55·10⁻⁷

Regarding the estimation of the acentric factor (ω) of these compounds, the common and most accurate technique to calculate this parameter is to estimate the critical constants (as discussed before) and use one experimental vapor pressure (P_v) such as that corresponding to T_b.[21] These authors recommend the use of the Pitzer expansion form[18,19] for the calculation of vapor pressure, defined by eq 4, using the expressions developed by Ambrose and Walton given by eqs 5 to 7.[20]

$$\ln P_{vr} = f^{(0)} + \omega \cdot f^{(1)} + \omega^2 \cdot f^{(2)} \quad (4)$$

$$f^{(0)} = (-5.97616 \cdot \tau + 1.29874 \cdot \tau^{1.5} - 0.60394 \cdot \tau^{2.5} - 1.06841 \cdot \tau^5) / T_r \quad (5)$$

$$f^{(1)} = (-5.03365 \cdot \tau + 1.11505 \cdot \tau^{1.5} - 5.41217 \cdot \tau^{2.5} - 7.46628 \cdot \tau^5) / T_r \quad (6)$$

$$f^{(2)} = (-0.64771 \cdot \tau + 2.41539 \cdot \tau^{1.5} - 4.26979 \cdot \tau^{2.5} - 3.25259 \cdot \tau^5) / T_r \quad (7)$$
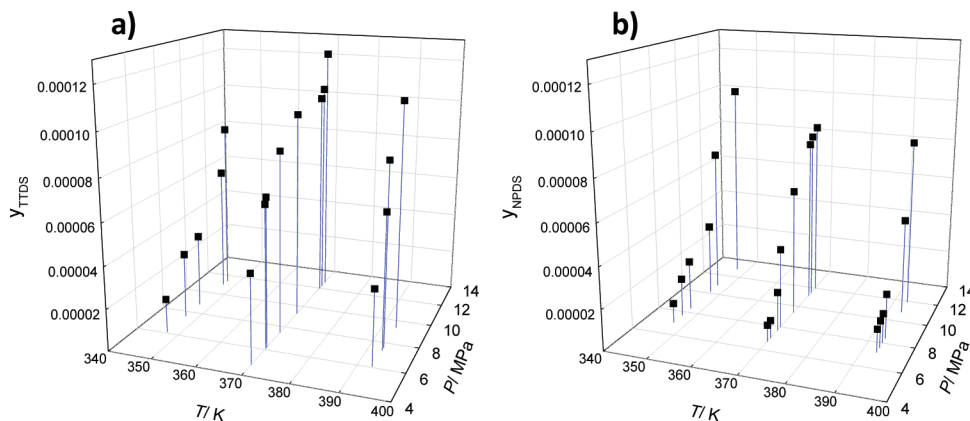
Figure 3. Experimental solubility in propane expressed as solute mole fraction (y_2). Subscript 2 corresponds to the solute: (a) TTDS, (b) NPDS.

where $\tau = (1 - T_r)$ and T_r is the reduced temperature ($T_r = T/T_c$). Since best results are obtained with reduced temperature (T_r) corresponding to T_b ($T_r = T_{br} = T_b/T_c$) according to Poling et al.,[21] T_{br} was used in these eqs 5 to 7 to calculate the acentric factor. Ignoring the term ω^2 (which is very close to zero for $T_r = T_{br}$) and solving for ω, eq 8 is obtained:

$$\omega = -\frac{\ln(P_c/1.01325) + f^{(0)}_{(T_{br})}}{f^{(1)}_{(T_{br})}} \qquad (8)$$

In this equation P_c is in bars, and T_b and T_c are absolute temperatures. The values of ω calculated by this technique for TTDS and NPDS are shown in Table 5.

Finally, to estimate the vapor pressure of the disulfide compounds as a function of temperature, the Ambrose–Walton corresponding states method defined by previous eqs 4 to 7 can be used.[20] These expressions allow obtaining the reduced vapor pressure ($P_{vr} = P_v/P_c$) at different values of the reduced temperature ($T_r = T/T_c$). The results of vapor pressure of TTDS and NPDS for temperature values studied experimentally in this work are summarized in Table 5.

4. RESULTS AND DISCUSSION

Tables 1 and 2 and Figure 3 show the solubilities of TTDS and NPDS in propane expressed as solute mole fraction, at the experimental conditions studied in this work. It can be observed that TTDS mole fraction in propane varies from $1.6 \cdot 10^{-5}$ to $1.2 \cdot 10^{-4}$ in the experimental range studied what is equivalent to (0.09 and 0.67) mg of solute per gram of propane. In case of NPDS, solute mole fractions are between $8.1 \cdot 10^{-6}$ and $1.0 \cdot 10^{-4}$, which correspond to (0.06 and 0.70) mg of solute per gram of propane. Although the solubility values of both compounds in propane are quite similar, TTDS presents slightly higher solubilities than NPDS at similar experimental conditions. It will be shown later in section 4.2 that it may be attributed to its higher vapor pressure and smaller molecular weight.

4.1. Effect of Pressure and Temperature in Solute Solubility. The influence of pressure on the solubility of both solutes is analogous: Increases of pressure at isothermal conditions lead to important increases in the solubility. Nevertheless, isobaric increases of temperature produce different tendencies in the solubility of these solutes. For TTDS, isobaric increases of temperature below 8 MPa lead to a maximum of the solubility at 370 K, whereas at 9 MPa increases of temperature always produce increases in the solubility. In the

case of NPDS at all pressures investigated, maximum values of the solubility were obtained at 370 K, this tendency being more marked for pressure values above 8 MPa.

These results are closely related to the influence of pressure and temperature on the density of the solvent and the solute vapor pressure, which are the main parameters affecting the solute solubility.[38,39] Specifically, the higher is the solvent density, the larger its solvent power and, consequently, the solute solubility; on the other hand, the higher the solute vapor pressure the larger its solubility.

Figure 4 shows the variation of propane density as a function of pressure and temperature in the experimental range
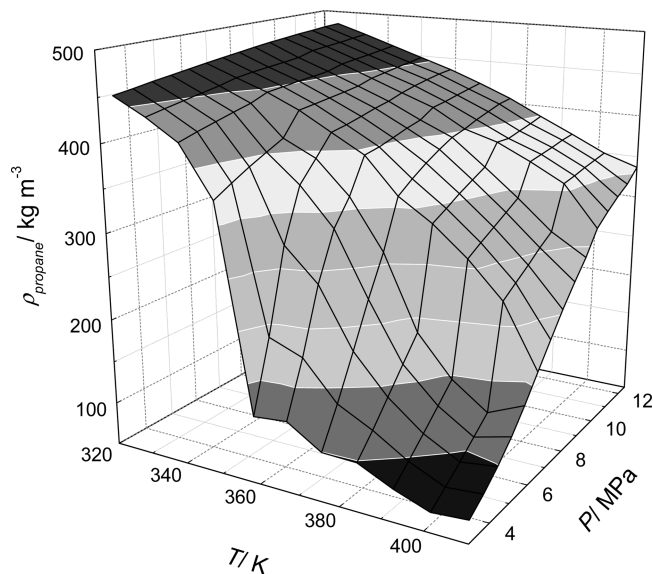

Figure 4. Variation of propane density ($\rho_{propane}$) with pressure and temperature in the experimental range investigated. Data obtained from the National Institute of Standards and Technology (NIST).[26]

studied.[26] This parameter increases with isothermal increases of the pressure; on the contrary, it decreases by increasing the temperature at constant pressure, this effect being stronger above the propane critical pressure and temperature. With regard to the solute vapor pressure, it increases exponentially with the temperature, as it can be observed in Table 5 for the solutes studied in this work (TTDS and NPDS).[20,21]

Bearing in mind all this, pressure increases must lead to solubility increases of the solutes in propane (because of the

higher propane density). However, increases of temperature may cause contrary effects: decreases in the solvent power due to the decrease of propane density, and increases in TTDS and NPDS solubility due to the higher solute vapor pressure.

According to the experimental results, it can be inferred that, for temperature values below the critical temperature, the effect of the solute vapor pressure on TTDS solubility dominates over that of solvent density, so temperature increases lead to higher solubilities. On the other hand, for temperature values over 370 K and pressures below 8 MPa, the abrupt decrease of propane density by increasing the temperature produces the decrease of solute solubility, the effect of solvent density being stronger than that of the TTDS vapor pressure. The same explanation can be extended to the influence of temperature on NPDS solubility in the entire pressure range studied. Nevertheless, it should be marked that NPDS vapor pressures are several orders of magnitude smaller than those of TTDS for the same temperature (see Table 5). This fact can explain that the temperature influences more importantly the solubility of TTDS than that of NPDS at isobaric conditions.

4.2. Comparison of TTDS and NPDS Solubility with That of Dibenzothiophene, Anthracene, and Carbazole in Propane. The experimental results reported in this work for the solubility of TTDS and NPDS in propane have been compared to those of different polyaromatic hydrocarbons (PAHs) in propane. Specifically, the solubility of anthracene (PAH), carbazole (nitrogen PAH), and dibenzothiophene (DBT, sulfur PAH) in propane is shown in Figure 5 together with that of
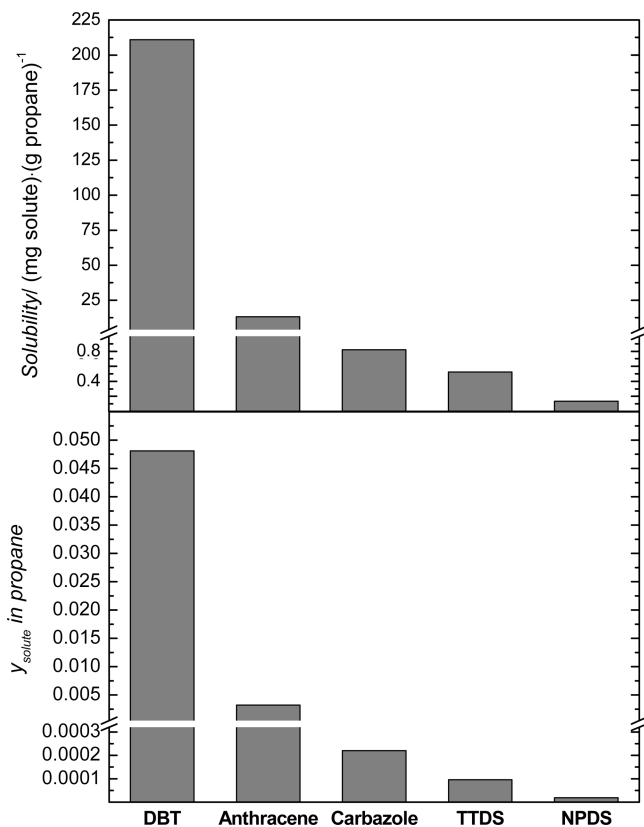

Figure 5. Comparison of DBT, anthracene, carbazole, TTDS, and NPDS solubility in propane at 370 K and pressure values in the range (7.5 to 7.9) MPa.

TTDS and NPDS. These values were obtained at 370 K and pressures between (7.5 and 7.9) MPa in all cases.[13−15] Given

that these solutes have different molar masses (see Table 6), the solubility has been expressed as solute mole fraction, but also in terms of mg of solute per gram of propane.

Large differences can be observed: NPDS and TTDS present the smallest values of solubility in propane (0.13 and 0.52 (mg solute)·(g propane)$^{-1}$), which are of the same order of magnitude than the solubility of carbazole (below 1 mg of solute per gram of propane). On the other hand, anthracene solubility is 1 order of magnitude larger than the previous ones, whereas DBT solubility is above 210 mg of solute per gram of propane.

These results may be explained taking into account the vapor pressure of the solutes and the interactions between the different solutes with the solvent (propane) which in turn, depend on their structure and polarity. Table 6 summarizes the molar masses (M), molecular structures, vapor pressures (P_v, at 370 K), and ground-state dipole moments (μ_g) of the solutes studied.

The calculation of the dipole moments of the different solutes has been carried out using the HyperChem computational chemistry package.[42] Geometry optimization of the molecules was performed using *Molecular Mechanics* with the *Amber2* force field.[43] The molecular structure that represents the potential minimum energy for each molecule was obtained using the Polak-Ribiere conjugate gradient method (with default values of parameters: rms energy gradient 0.1 ((kcal)·(Å·mol)$^{-1}$).[44] Subsequently, the dipole moment of the molecules was obtained (performing single point calculation) after application of AM1 semiempirical method with unrestricted Hartree−Fock (UHF) method.[45,46]
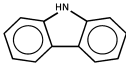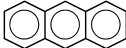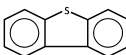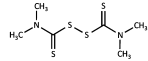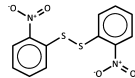
The solute vapor pressure is one of the main parameters affecting the solubility. The solutes with the largest vapor pressure values are TTDS and DBT, followed by anthracene, carbazole, and NPDS, which represents the smallest one. It is clear that the large solubility of DBT in propane is related to its high vapor pressure. In addition, the decreasing values of vapor pressure for anthracene, carbazole, and NPDS may explain their decreasing values of solubility in propane. Nevertheless, the large TTDS vapor pressure seems to be contradictory to its small solubility in propane, and, therefore other influencing factors must be considered.

It is well-known that nonpolar solvents dissolve preferably nonpolar solutes against polar ones. The solvent used in this study, propane, presents a molecular ground dipole moment near 0 (μ_g 0.084 D).[47] Thus, according to the molecular dipole moment of the solutes shown in Table 6, the affinity of the solutes with propane should follow the order: anthracene (μ_g 0.6 D) > DBT (μ_g 0.7 D) > NPDS (μ_g 0.9 D) > carbazole (μ_g 1.0 D) > TTDS (μ_g 3.9 D). Since TTDS presents the largest molecular dipole moment, it is the most polar compound among the solutes studied and, therefore, the one with the smallest affinity with propane. This observation could explain the low solubility of TTDS in propane, despite the fact that its vapor pressure is the highest among the solutes studied.

Finally, it should also be mentioned that, in general (for similar polarity and vapor pressure), organic molecules with small molecular weight should be more easily dissolved in supercritical fluids than those with higher molecular weights. This is consistent with the fact that NPDS presents the smallest solubility in propane (together with its smallest vapor pressure value), followed by TTDS (along with its large dipole moment).

4.3. Modeling of TTDS and NPDS Solubility in Propane by the Peng−Robinson Equation of State. The experimental values of the solubility obtained have been correlated to find mathematical expressions that allow the

Table 6. Values of the Molar Mass (M), Vapor Pressure at 370 K (P_v), and Ground Dipole Moment (μ_g) of the Solutes Compared

Solute	M^a/g·mol^{-1}	Structure	P_v (370 K)^b/ MPa	$\mu_g{}^c$/ D
Carbazole	167.208		$5.585 \cdot 10^{-07}$	1.0
Anthracene	178.230		$2.384 \cdot 10^{-06}$	0.6
DBT	184.26		$2.695 \cdot 10^{-05}$	0.7
TTDS	240.44		$4.58 \cdot 10^{-05}$	3.9
NPDS	308.34		$9.71 \cdot 10^{-08}$	0.9

^{a}Values taken from ref 23 ^{b}Values taken from ref 40: for carbazole 41, for anthracene 15, for DBT, and calculated in this work for TTDS and NPDS, by the Ambrose equation (ref 20). ^{c}Values taken from ref 42.

prediction of TTDS and NPDS solubility in propane at different operation conditions.

The Peng–Robinson equation of state (eq 9) can be used to predict the phase behavior of multicomponent systems.[16] Parameters $a(T)$ and b are defined by eqs 10 and 11.

$$P = \frac{R \cdot T}{\upsilon - b} - \frac{a(T)}{\upsilon \cdot (\upsilon + b) + b \cdot (\upsilon - b)} \tag{9}$$

$$a_i(T) = 0.45724 \cdot \frac{R^2 \cdot T_{C,i}^2}{P_{C,i}}$$

$$\cdot \left(1 + (0.37464 + 1.54226 \cdot \omega_i - 0.26992 \cdot \omega_i^2) \cdot \left(1 - \sqrt{\frac{T}{T_{C,i}}} \right) \right)^2 \tag{10}$$

$$b_i = 0.07780 \cdot \frac{R \cdot T_{C,i}}{P_{C,i}} \tag{11}$$

For multicomponent systems, mixture parameters a_M and b_M are estimated by the expressions given in eq 12. In these equations a_{ij} and b_{ij} represent the interaction parameters whose calculation is via mixing rules for which there are different sets reported in the literature.[13–16,48,49]

$$a_M = \sum_i \sum_j y_i \cdot y_j \cdot a_{ij} \qquad b_M = \sum_i \sum_j y_i \cdot y_j \cdot b_{ij} \tag{12}$$

The set of mixing rules used by Peng and Robinson[16] to estimate interaction parameters (a_{ij} and b_{ij}) was the one-fluid van der Waals set of rules, which is defined by eq 13 (where $k_{ij} = k_{ji}$, $k_{ii} = 0$). This set of mixing rules, labeled S1 in this work, implies the use of only one adjustable parameter (k_{ij}).

$$\text{S1:} \quad a_{ij} = \sqrt{a_i \cdot a_j} \cdot (1 - k_{ij})$$

$$b_{ij} = (b_1 + b_2)/2 \tag{13}$$

Likewise, a set of mixing rules involving two adjustable parameters (k_{ij} and δ_{ij}) has been used. It is labeled S2 and defined by eqs 14 (where $k_{ij} = k_{ji}$, $k_{ii} = 0$, $\delta_{ij} = \delta_{ji}$, $\delta_{ii} = 0$). This set has been used by our group in previous works yielding a good correlation of the experimental results.[13–15]

$$\text{S2:} \quad a_{ij} = \sqrt{a_i \cdot a_j} \cdot (1 - k_{ij})$$

$$b_{ij} = \sqrt{b_i \cdot b_j} \cdot (1 - \delta_{ij}) \tag{14}$$

To find the optimal values of the adjustable parameters, the Newton method has been used to minimize the average percentage deviation (APD), the objective function given by eq 15 that compares the experimental (y_2) and calculated (y_2^{cal}) solubility expressed as solute mole fraction (where subscript 2 corresponds to the solute, which are TTDS or NPDS in this work).

$$\text{APD} = \left(\sum_{i=1}^{n} \frac{|y_{2,i} - y_{2,i}^{cal}|}{y_{2,i}} \right) \cdot \frac{(100\%)}{n} \tag{15}$$

For each compound, the optimal values of the adjustable parameters of the Peng–Robinson equation with mixing rules sets S1 and S2, together with the APD values, are shown in Table 7. It can be observed that, for both solutes, the set of

Table 7. Optimal Values of the Adjustable Parameters of the Peng–Robinson Equation (Using Sets of Mixing Rules S1 and S2) for Modeling of TTDS and NPDS Solubility in Propane and Absolute Percentage Deviation (APD) between the Calculated and Experimental Solubility Values

mixing rules set	solute	parameter		APD/%
		k_{12}	δ_{12}	
S1	TTDS	0.4925		68.3
	NPDS	0.3983		75.8
S2	TTDS	1.1751	1.8195	22.4
	NPDS	1.0888	2.0844	18.4

mixing rules with only one parameter (S1) obtained APD values above 68 %, which is indicative of important differences
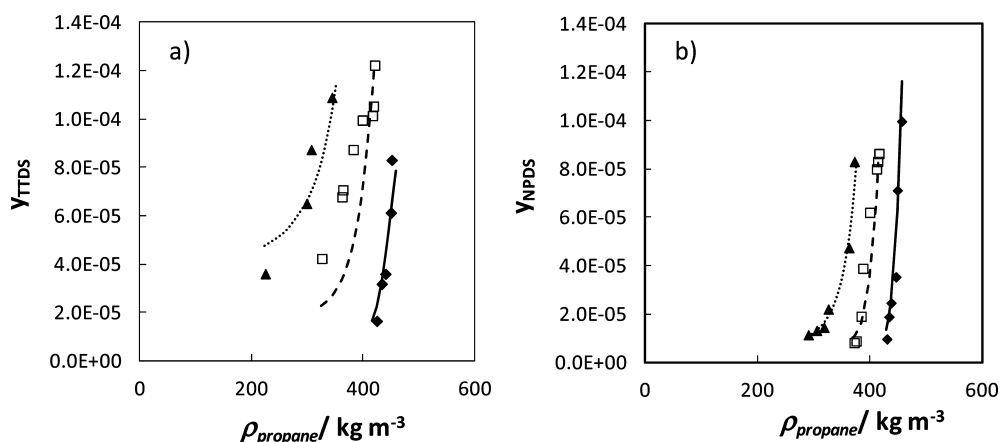
Figure 6. Comparison of the experimental solubility data with those estimated by the Peng–Robinson equation of state (using mixing rules set S2). Solute: (a) TTDS, (b) NPDS. Experimental solute mole fraction: ◆, 347 K; □, 370 K; ▲, 393 K. Lines represent solute mole fractions predicted by the Peng–Robinson equation of state: solid line, 347 K; dashed line, 370 K; dotted line, 393 K.

between the estimated and the experimental solubility data. On the other hand, the fitting of the experimental results obtained using the set of mixing rules S2 were significantly improved: the APD for TTDS was 22.4 %, and it was 18.4 % for NPDS. This improvement can be attributed to the fact that S2 involves the use of two adjustable parameters instead of one parameter used by S1. The fitting of the results for NPDS was better than that obtained for TTDS. Finally, to give a visual idea of the correlation, Figure 6 shows the estimated data together with the experimental for both solutes using the S2 set of mixing rules against propane density. In general a satisfactory fitting of the experimental results can be observed.

5. CONCLUSIONS

TTDS and NPDS solubilities in propane have been experimentally determined in a static view cell. In both cases, three values of temperature were studied: (347, 370 (critical temperature of propane), and 393) K. For TTDS (disulfide nitrogen hydrocarbon compound) the pressure varied from (4.8 to 12.7) MPa, and solubilities were in the range (0.09 to 0.67) (mg TTDS)·(g propane)$^{-1}$, which in the TTDS mole fraction corresponds to $1.6\cdot10^{-5}$ to $1.2\cdot10^{-4}$. In case of NPDS (disulfide nitrogen polyaromatic compound) the pressure range studied was (6.7 to 12.9) MPa, and solubilities varied from (0.06 to 0.70) mg of solute per gram of propane (NPDS mole fraction between $8.1\cdot10^{-6}$ and $1.0\cdot10^{-4}$).

For both solutes, isothermal increases of pressure lead to larger values of solubility, which can be attributed to the increase of propane density and its power solvent. It has also been found for NPDS and TTDS (for pressure values below 8 MPa) that when temperature is increased isobarically their solubilities present maximum values at the critical temperature of the solvent. It is known that two competing effects on solubility occur by increasing temperature: on one hand there is an increase of the solute vapor pressure, and on the other a decrease in the solvent density.

The comparison of the solubility of these compounds in propane with that of anthracene, carbazole, and DBT has been carried out at the same temperature and pressure conditions. It has been observed that the TTDS and NPDS solubility in propane is similar to that of carbazole and 1 and 2 orders of magnitude smaller than that of anthracene and DBT, respectively.

The critical constants, acentric factor, and vapor pressure of TTDS and NPDS (at experimentally studied temperatures) have been predicted by different estimation methods. These have not been reported in the literature previously. Calculated physical properties have been used in the modeling of the solubility by Peng–Robinson equation of state with two different sets of mixing rules. It has been observed that the set of mixing rules which involves the use of one adjustable parameter did not yield good results (APD above 68 % for both solutes), whereas satisfactory fitting of the experimental results (APD 22.4 and 18.4 for TTDS and NPDS) was obtained by using the set of mixing rules involving two adjustable parameters.

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