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Résumé — **Solubilité et coefficient de diffusion du sulfure d'hydrogène dans le polyéthylène glycol 400 de 100 à 140 ºC** — La limitation des rejets de gaz à effet de serre et de gaz acides, comme le sulfure d'hydrogène, est désormais une préoccupation majeure lors de la conception de procédés industriels. Dans ce contexte, Clauspol® est un procédé de traitement des gaz de queue du Claus qui répond à ce besoin en atteignant des taux de récupération en soufre élevés. Il consiste à convertir chimiquement H_2S et SO_2 en soufre élémentaire dans un solvant composé de polyéthylène glycol 400. L'optimisation de ce procédé requiert une connaissance précise de la solubilité et de la diffusivité des gaz dans ce solvant. Ainsi, ce travail présente dans le cas de H_2S des mesures expérimentales de ces grandeurs et leur modélisation dans les conditions opératoires du procédé. Les données de solubilité sont modélisées avec l'équation d'état de Sanchez-Lacombe avec un simple coefficient d'interaction binaire indépendant de la température. Les coefficients de diffusion sont déterminés en appliquant le modèle *Infinite-Acting* sur la courbe expérimentale de la chute de pression. Ils apparaissent être inversement proportionnels à la viscosité du solvant.

Abstract — **Solubility and Diffusion Coefficient of Hydrogen Sulphide in Polyethylene Glycol 400 from 100 to 140°C** — *The limitation of greenhouse and sour gas emissions in the atmosphere, such as hydrogen sulphide, is nowadays a major preoccupation in industrial processes. In this context, the Clauspol® process is a Claus tail gas treatment able to respond to this challenge of reaching high sulphur recovery. It consists of chemically converting H_2S and SO_2 into elementary sulphur in a polyethylene glycol 400 solvent. The optimisation of the process design requires a precise knowledge of both the solubility and diffusivity of these gases in this solvent. Hence, this work presents, in the case of H_2S, experimental measurements and modelling of these data in the process operating conditions. The solubility data are modelled by the Sanchez-Lacombe equation of state with a single temperature-independent binary interaction coefficient. The diffusion coefficients are determined by applying the Infinite-Acting model to the experimental pressure decay curve. It is found to be inversely proportional to the viscosity of the solvent.*

INTRODUCTION

The limitation of greenhouse and sour gas emissions in the atmosphere is nowadays a major preoccupation in industrial processes. In a refining plant, many rich hydrogen sulphide effluents are generated and have to be treated due to the high toxicity of this gas. The future specifications on the sulphur content of fuel blends will become more severe, and hydrotreatment units will consequently produce larger amounts of hydrogen sulphide. At the same time, the specifications on the global sulphur gases emitted into the atmosphere are becoming more and more restrictive. Therefore, the actual hydrogen sulphide treatment processes have to be improved in order to achieve these goals.

The Clauspol® process is one of the processes aiming to achieve a very high sulphur recovery [1-4]. It is a Claus tail gas treatment whose goal is to chemically convert hydrogen sulphide and sulphur dioxide into elementary sulphur and water, according to the reaction:

$$2 \, H_2S + SO_2 \leftrightarrow 3/x \, S_x + 2 \, H_2O \qquad (1)$$
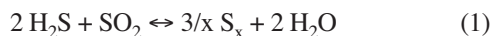
This reaction occurs in a non-volatile liquid organic solvent, polyethylene glycol 400 (PEG 400). Hydrogen sulphur and sulphur dioxide are absorbed in the solvent before reacting at a temperature slightly above the sulphur melting point, around 120°C. Hence, to simulate this process exactly and to improve its performance, it is necessary to know precisely some physical data, such as the solubility and the diffusivity of gas in the solvent.

In this work, we first present new experimental solubility data of hydrogen sulphide in PEG 400 between 100 and 140°C, *i.e.* in the process operating conditions range. These data are modelled with the Sanchez-Lacombe equation of state [5] with a single temperature-independent binary parameter. As the hydrogen sulphide contents are very low in the vapour phase, we focused on the Henry area of the phase diagram, and the Henry constants are predicted with this model. Secondly, the diffusion coefficient of H_2S in this solvent is experimentally estimated with the same apparatus. The methodology and the temperature dependence of this coefficient are highlighted.

1 EXPERIMENT

1.1 Apparatus and Material

The experimental setup used in this work has been described elsewhere [6, 7]. We only present here the main points of the apparatus schemed in Figure 1.
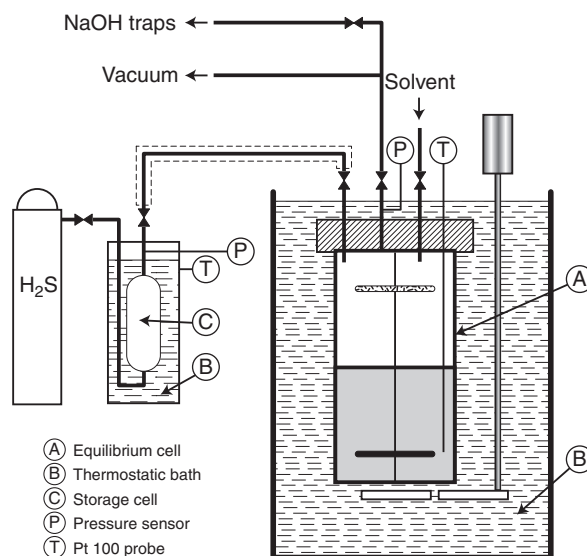

Figure 1

Experimental setup.

A 253.5-cm^3 static cell made of Hastelloy is immersed in a LAUDA thermostatic liquid bath whose temperature fluctuation does not exceed 0.05 K. Two stirring rotors ensure the homogeneity of liquid and vapour phases. Thermostated tubing links this equilibrium cell to a 169.1-cm^3 H_2S storage tank immersed in a thermostatic liquid bath. Additional tubing is used to link the equilibrium cell either to a vacuum system to allow the degassing of the solvent, or to sodium hydroxyl traps to securely clean the cell after each experiment. A Pt 100 probe measures temperature with an accuracy of 0.03 K. The pressure is measured with a HBM® 100 bar pressure sensor with an accuracy of 0.015 MPa or with a HBM® 20 bar pressure sensor with an accuracy of 0.0028 Mpa, depending on the experimental pressure range.

Hydrogen sulphide was provided by Air Liquid, with a purity of 99.7%. Polyethylene glycol 400 was provided by BASF. A Karl-Fisher titration indicated a water content of 0.34 weight percent in the polymer. Hence, a dehydration step is included in the experimental procedure described further.

1.2 Experimental Procedure

To measure solubility and estimate diffusion of H_2S in PEG 400, a three-step experimental procedure is performed.

The first step is the solvent dehydration in order to eliminate any traces of water dissolved in the commercial PEG 400. The equilibrium cell is filled with a well-known amount

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of solvent (around 100 g). The temperature is then increased to 120°C, and a vacuum is made in the cell for degassing it. At this temperature, the vapour pressure of polyethylene glycol 400 is about 1 Pa according to the manufacturer. Hence, no loss of polymer is expected during this purification step. From the vacuum pressure in the cell, P^{ini}, the residual dissolved water is estimated in terms of molar fraction, x_{water}, from Raoult's law:

$$x_{water} = \frac{P^{ini}}{P^{\sigma}_{water}(T)} \qquad (2)$$

where denotes the vapour pressure of water, computed from the DIPPR database [8]. Basically, this procedure allows one to decrease the water content by up to 0.04 weight percent.

The diffusion acquisition is the second step of the measurement. The temperature of the thermostated bath is adjusted to the desired operating temperature. No agitation of the cell is performed in this measurement procedure. At the initial time, a gas injection is performed and the pressure decay is recorded during a three-day period. The precise amount of hydrogen sulphide introduced, named $n^{0}_{H_2S}$ is determined by a mass balance in the storage bottle before and after the injection:

$$n^{0}_{H_2S} = \frac{V_{st}}{R}\left(\frac{P^{initial}_{st}}{Z(T^{initial}_{st}, P^{initial}_{st}) \cdot T^{initial}_{st}} - \frac{P^{final}_{st}}{Z(T^{final}_{st}, P^{final}_{st}) \cdot T^{final}_{st}}\right) \qquad (3)$$

where V, T and P denote volume, temperature and pressure, respectively. R is the ideal gas constant (R = 8.31451 J/mol/K), and Z the compressibility factor calculated from the Goodwin pure component equation of state [9]. The superscripts *initial* and *final* denote the time before and after the gas injection, respectively. The subscript *st* refers to the storage bottle. During the first two hours, the pressure in the cell is stored on a computer disk every five seconds. After that, it is stored every five minutes. The final pressure decay curve is exploited according to the model described further.

Finally, the third step of the experimental procedure is the hydrogen sulphur solubility measurements. Once the previously described three-day period is ended, the agitation rotors are started to completely reach thermodynamic equilibrium. The equilibrium pressure is noted, and a new gas injection is performed. The hydrogen sulphur amount injected is always calculated from the equation.

The amount of hydrogen sulphur dissolved in the solvent after each gas injection is determined by a mass balance:

$$n^{L}_{H_2S} = n^{0}_{H_2S} - n^{V}_{H_2S} \qquad (4)$$

where the superscripts L and V refer to the liquid and the vapour phases.

The amount of hydrogen sulphur in the vapour phase is calculated from the relation:

TABLE 1

Table of the experimental and calculated solubility of H₂S in PEG 400

T	P	× H₂S exp.	× H₂S calc.	AAD[1]
K	bar	mol.frac.	mol.frac.	%
373.15	1.18	0.062	0.057	6.97
373.15	2.75	0.128	0.126	2.01
373.15	4.43	0.190	0.190	0.34
373.15	6.03	0.243	0.244	0.41
373.15	7.29	0.280	0.283	0.98
373.15	8.31	0.308	0.312	1.27
393.15	1.83	0.070	0.066	5.93
393.15	3.87	0.133	0.132	0.84
393.15	5.87	0.189	0.189	0.33
393.15	7.04	0.218	0.219	0.66
393.15	8.53	0.252	0.256	1.29
393.15	9.59	0.276	0.280	1.38
413.15	1.81	0.049	0.051	4.44
413.15	3.16	0.084	0.087	3.23
413.15	4.56	0.119	0.121	1.44
413.15	6.02	0.152	0.154	1.80
413.15	7.18	0.177	0.179	1.53
413.15	8.68	0.208	0.210	1.14

[1] $AAD = \dfrac{|Exp.value - Calc.value|}{Exp.value} \cdot 100$

$$n_{vap} = \frac{P^{eq}_{cell} \cdot V^{V}}{Z(T_{cell}, P^{eq}_{cell}) \cdot R \cdot T_{cell}} \qquad (5)$$

where the superscript *eq* refers to the thermodynamic equilibrium state, and the subscript *cell* refers to the equilibrium cell. The vapour pressure of the solvent is assumed to be negligible.

The volume of the vapour phase is known from a volume balance:

$$V^{V} = V_{cell} - V^{L} \qquad (6)$$

The volume of the liquid phase is calculated from the mass and density of the solvent, assuming that the variation in volume due to the dissolved gas is negligible:

$$V^{L} = \frac{m_{s}}{\rho_{s}} \qquad (7)$$

where m_{s} is the mass of the solvent and ρ_{s} its density at the operating temperature. Preliminary work was done to determine the density of the dehydrated polyethylene glycol 400 used in this work according to the temperature:

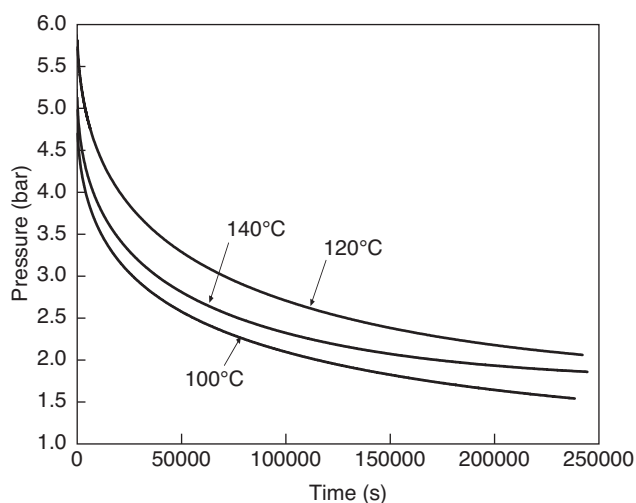$$\rho_{s}(kg/m^3) = -0.9037 \cdot T(K) + 1.394 \cdot 10^3 \qquad (8)$$

Figure 2

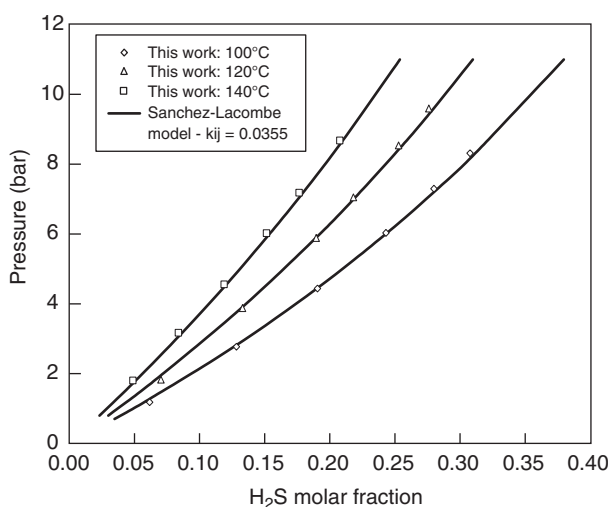Pressure decay measurement during H$_2$S diffusion in PEG 400 at 100, 120 and 140°C.

Figure 3

Experimental and calculated solubility of H$_2$S in PEG 400 at 100, 120 and 140°C.

1.3 Experimental Results

Three isotherms are investigated: 100, 120 and 140°C. For each isotherm, the pressure decay is measured, and a series of five additional injections are carried out. Figure 2 shows the pressure decay experimental curve for each temperature.

Figure 3 plots the hydrogen solubility for each isotherm for pressure from about 1 to 10 bar. The experimental points are listed in Table 1. There are no other data of H$_2$S solubility in PEG 400 available in the literature. Hence, no direct comparison or deviation estimation are possible. However, previous experiments on H$_2$S solubility in the same experimental setup, but in another solvent, have been reported in the literature [10]. The reproducibility of these experiments was estimated at about 2.5%. We assume here the same uncertainty for our experimental points.

2 SOLUBILITY MODELLING

H$_2$S solubility in PEG 400 is modelled with the Sanchez-Lacombe equation of state [5]:

$$\overline{P} = -\overline{T}\left[\ln\left(1-\overline{\rho}\right)+\left(1-\frac{1}{r}\right)\overline{\rho}\right]-\overline{\rho}^2 \tag{9}$$

where $\overline{P}$, $\overline{T}$ and $\overline{\rho}$ are the reduced pressure, temperature and density given by:

$$\overline{P} = \frac{Pv^*}{\varepsilon^*} \tag{10}$$

$$\overline{T} = \frac{RT}{\varepsilon^*} \tag{11}$$

$$\overline{\rho} = \rho r v^* \tag{12}$$

where ε^*, v^* and r are the microscopic parameters specific to each pure component, corresponding to the interaction energy between non-bonded molecular segments, the volume of a lattice site, and the number of lattice sites occupied by the molecule, respectively. For a mixture of c components, we adopt the following mixing rules:

$$v^* = \sum_{i=1}^{c}\phi_i v_{ii}^* \tag{13}$$

$$\varepsilon^* v^* = \sum_{i=1}^{c}\sum_{j=1}^{c}\phi_i\phi_j v_{ij}^*\varepsilon_{ij}^* \tag{14}$$

with

$$\phi_i = \frac{x_i r_i}{r} \tag{15}$$

$$v_{ij}^* = \frac{1}{2}\left(v_i^* + v_j^*\right) \tag{16}$$

$$\varepsilon_{ij}^* = \left(\varepsilon_i^*\varepsilon_j^*\right)^{1/2}\left(1-k_{ij}\right) \tag{17}$$

where k_{ij} is an empirical binary interaction parameter.

For polyethylene glycol 400, several sets of pure component parameters, adjusted on PVT data, are available. We choose to use the parameters proposed by Sanchez and Panayiotou [11]. For hydrogen sulphide, two sets of
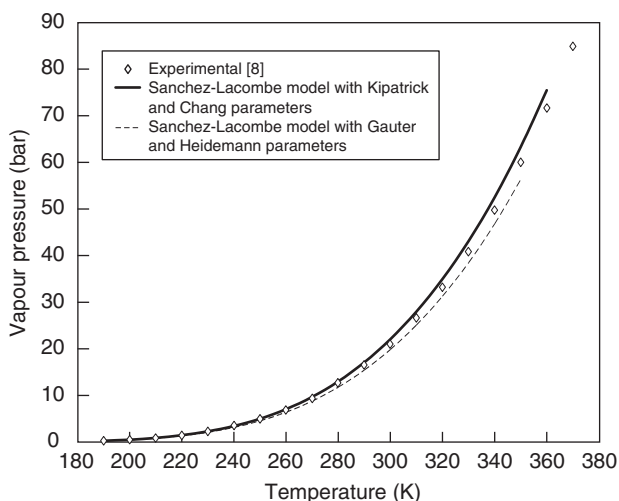
Figure 4

Experimental and calculated vapour pressure of pure H_2S. Experimental data are from the DIPPR database [8]. Modelled data are calculated with the Sanchez-Lacombe equation of state with the Kilpatrick and Chang [12] and the Gauter and Heidemann [13] parameter sets.

Figure 5

Experimental and calculated saturated liquid density of pure H_2S. Experimental data are from the DIPPR database [8]. Modelled data are calculated with the Sanchez-Lacombe equation of state with the Kilpatrick and Chang [12] and the Gauter and Heidemann [13] parameter sets.
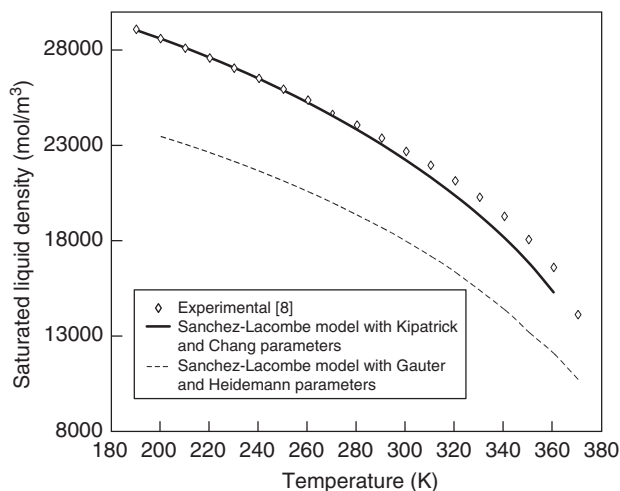
parameters are found: one proposed by Kilpatrick and Chang [12] adjusted on experimental data of the pure component properties, and another determined from a correlation proposed by Gauter and Heidemann [13] based on the critical

properties. As shown in Figures 4 and 5, it is found that the set proposed by Kilpatrick and Chang naturally allows a better prediction of both vapour pressure (deviation about 3%) and saturated liquid density (deviation about 2%) of pure H_2S. As a consequence, we choose to use this set of parameters for this compound. Finally, Table 2 resumes the pure-component Sanchez-Lacombe parameters used in this work.

TABLE 2

Pure-component Sanchez-Lacombe parameters of PEG 400 and H_2S

Compound	r	ε^* (J/mol)	v^* (m³/mol)	Ref.
PEG 400	30.35	5495.55	$1.1215.10^{-5}$	[11]
H_2S	6.3540	3076.48	$4.9080.10^{-6}$	[12]

Additionally, a binary interaction parameter is adjusted on our experimental data to reproduce them best. It is found that a single independent-temperature coefficient is sufficient to achieve a good accuracy. The optimal value is:

$$k_{H_2S/PEG400} = 0.0355 \qquad (18)$$

The modelled data are plotted in Figure 3 and reported in Table 1. The average deviation between model and experiments is globally about 2.0%.

The model performed being accurate at predicting the solubility data, it is used to calculate the Henry constant of H_2S in the solvent. By definition, the Henry constant is:

$$H_i = \lim_{x_i \to 0} \left(\frac{P\varphi_i y_i}{x_i} \right) \qquad (19)$$

where φ_i denotes the fugacity coefficient of the solute in the vapour phase, and x_i and y_i its molar fraction in the liquid and the vapour phases, respectively. As the solvent can be assumed to be non-volatile, the molar fraction of H_2S in the vapour phase is equal to one. The fugacity coefficient can be extracted from the Sanchez-Lacombe equation of state. Its analytic expression is the following [14]:

$$\ln \varphi_i = -\ln z + r_i \left[-2\frac{\overline{\rho}}{T} - \ln\left(1 - \overline{\rho}\right) \right] +$$
$$\left(\frac{z-1}{r} \right) \left[\frac{nr}{v^*} \left(\frac{\partial v^*}{\partial n_i} \right)_{n_j} \right] - \frac{\overline{\rho}}{T} \left[\frac{nr}{\varepsilon^*} \left(\frac{\partial \varepsilon^*}{\partial n_i} \right)_{n_j} \right] \qquad (20)$$

with

$$z = \frac{Pv}{RT} \qquad (21)$$

$$n = \sum_{i=1}^{c} n_i \qquad (22)$$

$$r = \sum_{i=1}^{c} x_i r_i \tag{23}$$

Hence, the fugacity coefficient at infinite dilution (*i.e.* when the concentration of the solute leads to zero) is given by:

$$\ln\varphi_i^\infty = -\ln z^\infty + r_i \left[-2\frac{\overline{\rho}^\infty}{\overline{T}^\infty} - \ln\left(1 - \overline{\rho}^\infty\right) \right] + \left(\frac{z^\infty - 1}{r_s}\right) \lim_{n_1 \to 0} \left[\frac{nr}{v^*}\frac{\partial v^*}{\partial n_i}\right] - \frac{\overline{\rho}^\infty}{\overline{T}^\infty} \lim_{n_1 \to 0} \left[\frac{nr}{\varepsilon^*}\frac{\partial \varepsilon^*}{\partial n_i}\right] \tag{24}$$

where, with the chosen mixing rules:

$$\lim\left[\frac{nr}{v^*}\frac{\partial v^*}{\partial n_i}\right] = \frac{1}{v_s^*}\left[r_i\left(-v_s^* + v_i^*\right)\right] \tag{25}$$

$$\lim\left[\frac{nr}{\varepsilon^*}\frac{\partial \varepsilon^*}{\partial n_i}\right] = \frac{1}{\varepsilon_s^* v_s^*}\left[2r_i\left(-\varepsilon_s^* v_s^* + \frac{1}{2}\sqrt{\varepsilon_s^*\varepsilon_i^*}\left(1 - k_{is}\right)\left(v_s^* + v_i^*\right)\right)\right] - \frac{1}{v_s^*}\left[r_i\left(-v_s^* + v_i^*\right)\right] \tag{26}$$

$$\overline{\rho}^\infty = \frac{r_s v_s^*}{v_s^\sigma} \tag{27}$$

$$\overline{T}^\infty = \frac{RT}{\varepsilon_s^*} \tag{28}$$

$$z^\infty = \frac{P_s^\sigma v_s^\sigma}{RT} \tag{29}$$

The saturated molar volume of the pure solvent v_s^σ is computed from the equation of state. Finally, the Henry constants of hydrogen sulphide in polyethylene glycol for the three temperatures investigated are given in Table 3. According to the uncertainty of the experimental data and the precision of the model, we assume an uncertainty of about 5% for these Henry constant values.

TABLE 3

Henry constant of H_2S in PEG 400 at 100, 120 and 140°C

T (K)	H (bar/mol.frac.)
373.15	19.59
393.15	26.15
413.15	33.65

3 DIFFUSION COEFFICIENT MODELLING

The diffusion coefficient is determined with an inverse problem methodology, in which the experimental data can be reproduced on the basis of unknown parameters. In our case, the unknown parameter is the diffusion coefficient, and the experimental data are the pressure decay curve. The model used to reproduce this curve is the so-called Infinite-Acting model, largely described by Sheikha *et al.* [15] in their bibliographic review of diffusion coefficient determination methodologies. The assumptions of the methodology are the following: the system is non-reactive, isothermal conditions are assumed throughout the pressure decay experiment, the solvent is non-volatile, the diffusion coefficient is constant, there is only a diffusion phenomenon which follows Fick's second law, the Henry law can be applied to the gas-liquid equilibrium at the interface, and the liquid phase is a semi-infinite medium.

Following Fick's second law:

$$D\frac{\partial^2 C(z,t)}{\partial z^2} = \frac{\partial C(z,t)}{\partial t} \tag{30}$$

where D is the diffusion coefficient, and $C(z,t)$ the dissolved gas concentration in the liquid phase at the depth z in the liquid phase (origin is taken at the gas-liquid interface) and at the time t.

A mass balance at the interface ($z = 0$) gives:

$$-V_g\frac{\partial C_g(t)}{\partial t} = -SD\left(\frac{\partial C(z,t)}{\partial z}\right)_{z=0} \tag{31}$$

where V_g is the volume of the vapour phase, calculated from the equation, $C_g(t)$ the gas concentration in the vapour phase, and S the surface of the gas-liquid interface known from the geometry of the equilibrium cell.

The Henry law at the gas-liquid interface is:

$$H = \frac{P}{\overline{v} \cdot C(0,t)} \tag{32}$$

where $\overline{v}$ is the molar volume of the liquid phase, assumed to be equal to the molar volume of the solvent (as for the solubility data calculation methodology, the variation in volume due to the dissolved gas is neglected).

With the relation:

$$P = Z(T,P)\,C_g(t)\,RT \tag{33}$$

the Henry law expression is equivalent to:

$$C_g(t) = \alpha \cdot C(0,t) \tag{34}$$

with

$$\alpha = \frac{H\overline{v}}{Z(T,P)\,RT} \tag{35}$$

This differential equations system is solved using the Laplace transforms. In the mathematical resolution, it is assumed that the α parameter does not depend on the time.

Because the pressure difference between the initial and the final time of the pressure decay curve is relatively small (3 bar at max.), this assumption is realistic. Rigorously, after the initial degassing process, the pressure in the cell is equal to the vapour pressure of the solvent P_b. Because of the extremely low volatility of PEG 400, it is in fact the vapour pressure of the traces of water in this solvent. Therefore, it is necessary to work with relative pressures. Finally, the expression of pressure as a function of time is:

$$\frac{P(t)-P_b}{P(0)-P_b} = \frac{Z(T,P(t))}{Z(T,P(0))}\exp\left(\phi^2\right)\cdot erfc\left(\phi\right) \qquad (36)$$

where $P(0)$ is the pressure just after the gas introduction, and with:

$$\phi = \sqrt{\frac{Dt}{\alpha^2 L^2}} \qquad (37)$$

and L is the height of the vapour phase, calculated with:

$$L = \frac{V_g}{S} \qquad (38)$$

At this step, the methodology consists of fitting the coefficient diffusion in order to reproduce well the experimental pressure decay curve. However, due to the non-linearity of the equation, the adjustment method is complex. Thus, we should modify equation to obtain a linear form. Moreover, it is important to note that this Infinite-Acting model gives for an infinite time a pressure equal to zero and not, as we can expect, equal to the equilibrium pressure. Hence, this model cannot be used in the whole range of time, and has to be employed only at the beginning of the pressure decay curve. The linearisation of equation must allow one to easily determine the validity range of the model.

In this way, we use the methodology proposed by Sheikha *et al.* [16], consisting of using a development of the *erfc* function. Indeed, following the mathematical form proposed by Abramovitch [17]:

$$erfc(x) = \left(a_3\left[\beta(x)\right]^3 + a_2\left[\beta(x)\right]^2 + a_1\beta(x)\right)\exp(-x^2) + \varepsilon \qquad (39)$$

with

$$\beta(x) = \frac{1}{a_4 x + 1} \qquad (40)$$

and $a_1 = 0.3480242$, $a_2 = -0.0958798$, $a_3 = 0.7478556$, $a_4 = 0.47047$, $|\varepsilon| < 2.5.10^{-5}$. Reporting that in equation, we find:

$$\frac{P(t)-P_b}{P(0)-P_b}\cdot\frac{Z(T,P(0))}{Z(T,P(t))} = \left(a_3\left[\beta(\phi)\right]^3 + a_2\left[\beta(\phi)\right]^2 + a_1\beta(\phi)\right) \qquad (41)$$

Such an equation can be reformulated in:

$$a\phi^3 + b\phi^2 + c\phi + d = 0 \qquad (42)$$

with:

$$a = a_4{}^3\left(\frac{P(t)-P_b}{P(0)-P_b}\right)\frac{Z(T,P(0))}{Z(T,P)} \qquad (43)$$

$$b = 3a_4{}^2\left(\frac{P(t)-P_b}{P(0)-P_b}\right)\frac{Z(T,P(0))}{Z(T,P)} - a_1 a_4{}^2 \qquad (44)$$

$$c = 3a_4\left(\frac{P(t)-P_b}{P(0)-P_b}\right)\frac{Z(T,P(0))}{Z(T,P)} - a_2 a_4 - 2a_1 a_4 \qquad (45)$$

$$d = \left(\frac{P(t)-P_b}{P(0)-P_b}\right)\frac{Z(T,P(0))}{Z(T,P)} - a_3 - a_2 - a_1 \qquad (46)$$

Equation 42 has only one real root. For each time t, this root, ϕ, is found in solving this equation and the curve giving this root as a function of the square root of time is plotted. According to the relation (37), this curve should be a straight line passing through the origin. An example of such a curve is shown in Figure 6, for the experimental measurements at 140°C. Similar curves are obtained for the two other temperatures investigated (100 and 120°C).

Then, knowing the Henry constant at the operating temperature *(Table 3)* and the geometry characteristics of the cell, the slope of this curve in its linear part directly gives the diffusion coefficient. Moreover, the time limit above which the Infinite-Acting model can no longer be applied is identified when this curve can no longer be considered as a straight line. For example, in Figure 6, we can see that the experimental curve can no longer be considered as linear from a
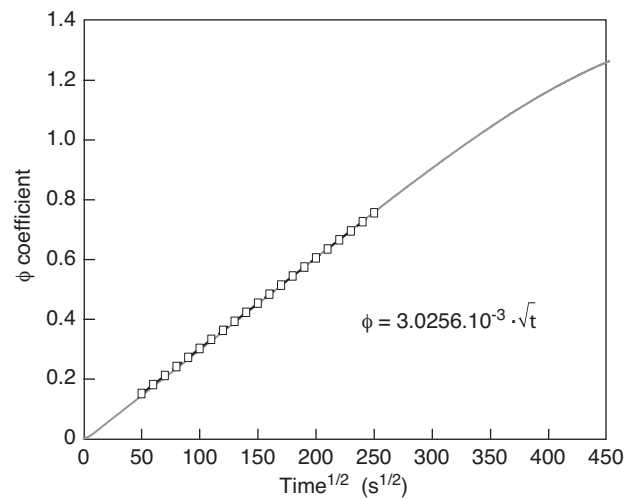

Figure 6

Evolution of the real root, ϕ, of Equation 43 *versus* time (solid light line), and linear regression of the linear part of this curve (dotted dark line with open squares) at 140°C.

square root of time of about 350 $s^{1/2}$. This example shows that we consider a decay of pressure by a factor of around 2 to deduce the diffusion coefficient. Hence, not only the initial slope of the pressure decay curve is used. Moreover, in this example, after 34 hours the curve still follows Fick's law, and no convection phenomenon is noticed. For each temperature, the calculated diffusion coefficient is summarised in Table 4. With this methodology, the diffusion coefficient appears to be very sensitive to the Henry constant value. According to the uncertainty of our previously determined Henry constants, we assume an uncertainty of about 10% in the diffusion coefficient. It is also important to note that according to the large number of assumptions and the simplification in the mathematical treatment of the curve, these values cannot be considered as rigorous measurements of the diffusion coefficient, but only as estimations.

TABLE 4

Diffusion coefficient of H_2S in PEG 400 at 100, 120 and 140°C

T (K)	$10^9 D$ (m^2/s)
373.15	1.6853
393.15	2.2270
415.15	3.6214

In Figure 7, the diffusion coefficient is plotted as a function of the viscosity of the solvent. This last property is calcu-
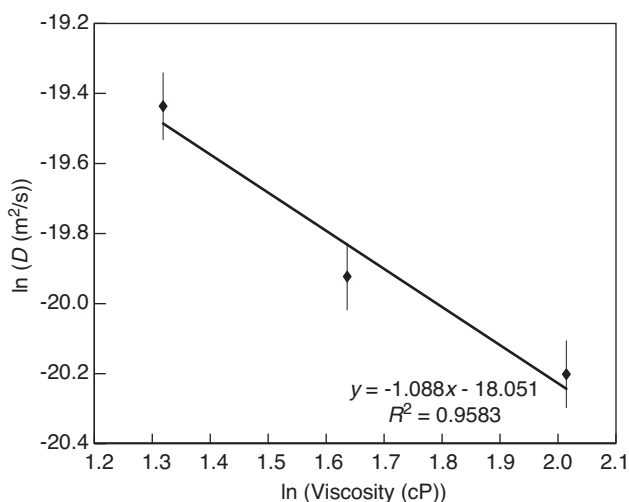
lated for the three temperatures investigated from the correlation proposed by Cruz *et al*. [18], after having preliminarily checked with some experiments that it is applicable to the PEG 400 used in this work.

Taking into account the experimental uncertainties, this figure shows that the diffusion coefficient of hydrogen sulphide in PEG 400 is inversely proportional to the viscosity of the solvent. This observation is consistent with the Stockes-Einstein equation, which gives the general form of the theoretical evolution of the diffusion coefficient with viscosity based on hydrodynamic theory, and which states the inversely proportionality relation between these physical properties [19].

CONCLUSION

In this work, new experimental data of the solubility and diffusion coefficient of hydrogen sulphide in PEG 400 were measured from 100 to 140°C. The solubility data are accurately modelled with the Sanchez-Lacombe equation of state with a single temperature-independent binary interaction coefficient. Simultaneously, the diffusion coefficients are estimated by applying the Infinite-Acting model to the experimental pressure decay curve. They are found to be inversely proportional to the viscosity of PEG 400.

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Figure 7

Variation in the diffusion coefficient of H_2S in PEG 400 with the viscosity of the solvent.

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