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Chemical Engineering Journal 138 (2008) 172–178

Chemical Engineering Journal

www.elsevier.com/locate/cej

Determination of ozone solubility in polymeric materials

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Received 25 January 2007; received in revised form 1 June 2007; accepted 19 June 2007

Abstract

The transport of a gas or vapour through a dense, nonporous membrane can be described in terms of a solution-diffusion mechanism, which states that the permeability is determined by its diffusivity and solubility. The solubility of many different molecules in many different polymers has been measured and can be found in the literature. However, very little information can be found about the solubility of ozone in polymers. Therefore, a dynamic frontal chromatography method to determine the ozone solubility was developed and was successfully applied to three different polymers: Teflon 65 N ($S = 0.088 \pm 0.080$ mole O_3/m^3 polymer per mole O_3/m^3 air at $T = 296.95$ K, $n = 3$), "reaction exhausted" polydimethylsiloxane (PDMS) ($S = 1.005 \pm 0.077$ mole O_3/m^3 polymer per mole O_3/m^3 air at $T = 298.85$ K, $n = 5$) and Hyflon AD80 ($S = 3.549 \pm 0.147$ mole O_3/m^3 polymer per mole O_3/m^3 air at $T = 298.15$ K, $n = 4$). The term "reaction exhausted" PDMS polymer is used, because initially a reaction was observed and sorption values could only be determined after this reaction was exhausted. Experiments were performed at different temperatures; sorption proved to be strongly temperature dependent, for "reaction exhausted" PDMS a ΔH_s value of -11.05 ± 0.98 (standard deviation) kJ/mole was measured ($n = 8$); for Hyflon AD80 a ΔH_s value of -17.24 ± 1.17 (standard deviation) kJ/mole was measured ($n = 8$). The quantitative ozone solubility data presented here are of high relevance to polymeric membrane-assisted processes, which make use of ozone as an oxidant, for example, advanced oxidation processes (AOP's).

Keywords: Absorption; Desorption; Polymers; Chromatography; Ozone; Membranes

1. Introduction

Advanced oxidation processes (AOPs) have become the subject for many researchers for environmental applications. AOPs generate highly reactive hydroxyl radicals that enable complete oxidation of organic compounds at near ambient temperature and pressure [1]. Initially AOP's were developed for water purification purposes, but recently the interest appeared to use them in air purification applications as well [2–4]. Some of the AOPs (e.g. the Peroxone process) use ozone for the production of the hydroxyl radicals.

Another technology that is of increasing interest for use in air purification applications is membrane technology. Several researchers reported experimental results for membrane-aided removal of components like H_2S, CO_2 or volatile organic compounds (VOCs) from waste gas streams [5–8]. This membrane technology can be combined with ozone or AOP technology to develop waste gas purification [9].

A number of membrane applications use a dense polymer layer. This can be in the form of a total dense membrane or as a thin dense skin layer on a porous support. As transport through dense materials is given by the solution diffusion process, the membrane polymer type is of major importance in this case. Both solubility and diffusivity for the combination component/membrane polymeric material determine the permeability. A high permeability is advantageous for the process efficiency, resulting in limited membrane area and a compact installation.

Although some literature about ozone/polymer interaction is available [10–12], no data on absorption of ozone into polymers could be found. Only ozone adsorption data onto inorganic particles has been reported in [13,14].

Today different methods are available to measure the solubility of gases or vapours in polymers or liquids. The most common used methods are the pressure decay method [15], the gravimetrical method [15], static headspace methods like equilibrium partitioning in closed systems (EPICS) [16] or vapour phase calibration (VPC) [17] or dynamic chromatographic column methods [13]. The pressure decay method and static headspace methods are not suitable to measure ozone solubility in polymers. Both methods assume that the decrease in headspace

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doi:10.1016/j.cej.2007.06.012

Nomenclature

List of symbols

C_M	equilibrium concentration of the compound in the mobile phase (mole/m^3 MP)
C_S	equilibrium concentration of the compound in the stationary phase (mole/m^3 SP)
C_t	outlet ozone concentration during a sorption experiment (g O_3/m^3)
$C_{\mathrm{t}=0}$	outlet ozone concentration at the start of a sorption experiment (g O_3/m^3)
$C_{\mathrm{t}=\infty}$	constant outlet ozone concentration at the end of a sorption experiment (g O_3/m^3)
D	diffusion coefficient (m^2/s)
ΔH_s	enthalpy of sorption (kJ/mole)
k_n	variable n in the simulation
k'	capacity factor (-)
m_polymer	mass of polymer in the column (kg)
n	number of experimental repetitions (-)
P	permeability coefficient (m^2/s)
Q_i	flow rate in volume V_i (m^3/s)
R	ideal gas constant (J mol^{-1} K^{-1})
S	solubility coefficient (mole O_3/m^3 polymer per mole O_3/m^3 air)
t	time (s)
t_extra	ozone retention time in front and after the column (s)
t_M	dead time (hold up time) in the column (s)
t_R	ozone retention time in the column (s)
$t_\mathrm{retention\ empty\ column}$	retention time in the overall system with an empty column (s)
t_total	ozone retention time in the overall system (s)
T	temperature (K)
V_1	volume between 4-way valve and column (m^3)
V_2	volume of the empty column (m^3)
V_3	volume in between column and ozone analyser (m^3)
V_4	analyser volume (m^3) (real physical volume and response time effects)
V_M	volume of the mobile phase in the column (m^3)
V_S	volume of the stationary phase in the column (m^3)
ρ_polymer	polymer density (kg/m^3)
β	phase ratio (-)

concentration can be fully attributed to sorption of that gas or vapour in the polymer or liquid. If one would apply one of these methods for ozone, a decrease in ozone headspace concentration is not necessarily the result of sorption, but can also be caused by reaction with the polymer or self-decomposition in function of time. Also the gravimetrical method is not an option. In this method a sample of polymer or liquid is brought into contact with a certain concentration of gas or vapour. The mass of the polymer or liquid sample is monitored in function of time until equilibrium is reached. For a reactive molecule like ozone the mass of the polymer is not a suitable measure for sorption, because a possible reaction between ozone and the polymer can also alter its mass.

For the reasons mentioned above, a dynamic frontal chromatography method was developed. This dynamic method reduces the time of the experiments minimizing the decay of ozone. Secondly, if properly designed, the method allows one to make a clear distinction between absorption phenomena and ozone decay by reaction between ozone and the polymer material by comparison of absorption and desorption concentration profiles. The different aspects of the method are discussed below.

2. Experimental

2.1. Experimental setup

In Fig. 1, the experimental setup is drawn schematically. The carrier gas used for all the experiments is dry air (Alphagaz 1, Air Liquide). The main airflow is split into two equal airflows both controlled by mass flow controllers (MFC 1:UCAR; MFC 2: Bronckhorst). The outlet of the ozone generator is connected with the UCAR mass flow controller. Before entering the 4-way valve (Whitey), both flows go through a water bath with a controlled temperature (Lauda A100). After the 4-way valve, one of the two flows is sent to the column, the other one bypasses the column. In the bypass over the column there is a valve (Nupro) for controlling the pressure drop over the bypass. The column used is a glass cylinder, which has a shell side and a lumen side. In the lumen, the polymer particles can be brought and in the shell side, water of a certain temperature is recirculated to control the temperature of the column. Only glass, Teflon and stainless steel are used as materials. The outlet of the column is directly connected to a UV-ozone analyser (Anseros Ozomat GM). Data logging of the ozone analyser signal is done by an analog to digital converter (ADC 16, Pico Technology limited) to a PC. All inlet ozone concentrations in the experiments were observed to be in between 0.3 and 0.8 g/m^3.

2.2. Polymers

An overview of the different polymers used and their characteristics are given in Table 1. The polymers, for which the sorption was determined, are all in the suitable particle size range. The particle size has to be small enough, to assure that the sorption equilibrium is reached, when an absorption experiment is terminated. To check whether the polymer is in the right particle size range, a minimum experimental time is calculated with formulas based on nonstationary mass transfer [18,19]. This value is tested in experiments, which investigate the experimental result in function of the time. In the approach described above, knowledge of the diffusion coefficient of ozone in the different polymers is very important. To estimate these diffusion coefficients, correlations were used which plot the logarithm of the critical volume of different molecules in function of the logarithm of the diffusion coefficient. Information used to estimate the diffusion coefficients of ozone in the different polymers applied in this study were found in [20] for PTFE and in [21] for Polydimethylsiloxane (PDMS) and Hyflon AD80.

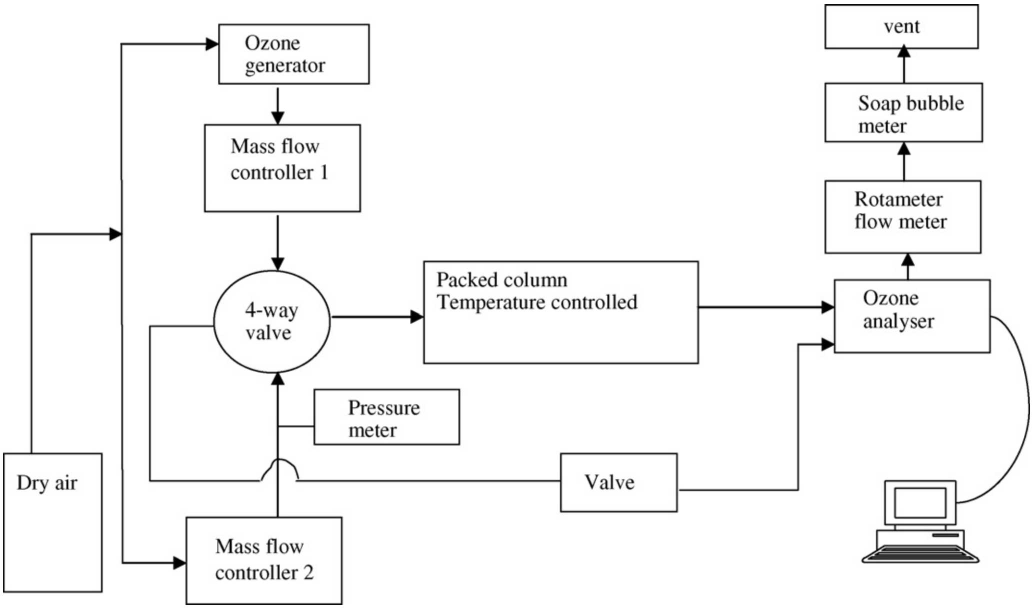

Fig. 1. Experimental setup scheme.

2.3. Determination of the solubility

2.3.1. Calculation and procedure to determine the solubility coefficient

The following formula for description of mobile/stationary phase equilibrium distribution is obtained (gas/liquid) [22]:

$$S = \frac{C_S}{C_M} = k' \times \beta = k' \times \frac{V_M}{V_S} \qquad (1)$$

The capacity factor k' is described by the following formula:

$$k' = \frac{t_R - t_M}{t_M} \qquad (2)$$

Combining formula's (1) and (2) gives:

$$S = \frac{t_R - t_M}{t_M} \times \frac{V_M}{V_S} \qquad (3)$$

Table 1
Polymer characteristics

Polymer	Characteristics
Teflon 65 N	Teflon 65 N was received from the DuPont company (Dordrecht, The Netherlands). It is one of DuPont's PTFE fine powder resins for paste extrusion. The degree of cristallinity of the polymer was determined with differential scanning calorimetry (DSC) and was observed to be 28%. Particle size analysis results with a Malvern Mastersizer (laser diffraction measuring technique) from the Teflon 65 N powder gave a mean aggregate D43 diameter of 749 ± 38 μm ($n = 3$). Scanning electron microscopy (SEM) analysis showed that the aggregates consist of small spheres with a diameter of about 0.5 μm.
Polydimethylsiloxane (PDMS)	Homogeneous PDMS membranes were prepared in the laboratory of Prof. Vankelecom (university of Leuven, Belgium). The PDMS sheets were synthesized by crosslinking a prepolymer RTV615A and a crosslinker RTV615B (General Electric) in *n*-heptane for 30 min at 70 °C in a heated oil bath. The cooled PDMS solution was subsequently poured in petridishes to obtain self-supporting PDMS membranes. Afterwards, the transparent film obtained was transformed in smaller rectangular pieces (about 0.5–1.0 cm^2) by cutting them manually. The ozone solubility values are determined after the initially observed reaction is exhausted. The thickness of the different pieces ranged from a few hundred micrometers to 1 mm. Initially, a reaction is observed and sorption values were measured after the reaction is exhausted. Therefore, the sorption values are linked to "reaction exhausted" PDMS instead of "neat" PDMS.
Hyflon AD80	Hyflon AD80 amorphous perfluoropolymer was received as a white powder from the Solvay Solexis company (Bollate (Milano), Italy). It is a copolymer consisting of 80 mol % 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) and 20 mol % tetrafluoroethylene (TFE). Particle size analysis results with a Malvern Mastersizer (laser diffraction measuring technique) from the Hyflon AD80 powder gave a mean aggregate D43 diameter of 465 ± 19 μm ($n = 2$). Scanning electon microscopy (SEM) analysis showed that the aggregates consist of porous polymer blocks with a maximum diameter of about 200 μm.
HDPE polymer	High density polyethylene (HDPE) polymer was received as white powder from the Centexbel company (Ghent, Belgium). The exact polymer composition was not given by the polymer supplier.

In the experimental setup, ozone retention in the overall system (t_{total}) will be determined by the total retention in the column (t_{R}) and the residence time in front and after the column (t_{extra}):

$$t_{\mathrm{R}} = t_{\mathrm{total}} - t_{\mathrm{extra}} \tag{4}$$

To determine t_{extra} the experimental setup after the 4-way valve is divided into four volumes: volume between 4-way valve and column (V_1 in m^3), the column (V_2 for the empty column in m^3), volume in between column and ozone analyser (V_3 in m^3) and volume in the analyser between inlet and measuring cuvette, with possible response time effects included (V_4 in m^3). In this way, t_{extra} (s) can be written as follows:

$$t_{\mathrm{extra}} = t_1 + t_3 + t_4 = \frac{V_1}{Q_1} + \frac{V_3}{Q_3} + \frac{V_4}{Q_4} \tag{5}$$

The volume of the stationary phase V_{S} (m^3) can be written as:

$$V_{\mathrm{S}} = \frac{m_{\mathrm{polymer}}}{\rho_{\mathrm{polymer}}} \tag{6}$$

With $V_{\mathrm{M}} = V_2 - V_{\mathrm{S}}$ and $t_{\mathrm{M}} = V_{\mathrm{M}}/Q_2 = (V_2 - V_{\mathrm{S}})/Q_2$, one obtains

$$S = \left(\frac{\rho_{\mathrm{polymer}} \times Q_2}{m_{\mathrm{polymer}}}\right) \times \left(t_{\mathrm{total}} - \left(\sum_{i=1}^{4} \frac{V_i}{Q_i}\right) + \frac{m_{\mathrm{polymer}}}{Q_2 \times \rho_{\mathrm{polymer}}}\right) \tag{7}$$

The volume V_4 (volume analyser and possible response time effects) was calculated with the following formula:

$$V_4 = Q_4 \times \left(t_{\mathrm{retention\ empty\ column}} - \left(\frac{V_1}{Q_1}\right) - \left(\frac{V_2}{Q_2}\right) - \left(\frac{V_3}{Q_3}\right)\right) \tag{8}$$

where $t_{\mathrm{retention\ empty\ column}}$ is t_{total} with an empty column. V_4 was observed to be flow rate dependent, probably due to some response time effect of the analyser.

At the beginning of every experiment, both a flow of pure air and an ozone/air mixture are sent to the 4-way valve. Before the absorption experiment starts, the stream of pure air is lead over the column, while the ozone containing stream goes directly over the bypass to the vent. At the start of an absorption experiment, the 4-way valve is switched and a mixture of air and ozone enters the column. The experiment finishes if the column outlet ozone concentration reaches a plateau (note that the experimental time should be high enough to reach a uniform ozone concentration in the polymer). Directly after this absorption experiment, the 4-way valve is switched again and now pure air is sent over the column, which removes all the ozone present in the column. This is the desorption experiment. The typical profiles of an absorption and desorption experiment are given in Fig. 2a (Teflon 65 N polymer). With formulas (9) and (10) a total retention time can be calculated. The integration is done by the Simpson method.

$$t_{\mathrm{total\ absorption}} = \int \left(\frac{C_{\mathrm{t}=\infty} - C_{\mathrm{t}}}{C_{\mathrm{t}=\infty} - C_{\mathrm{t}=0}}\right) \times \mathrm{d}t \tag{9}$$

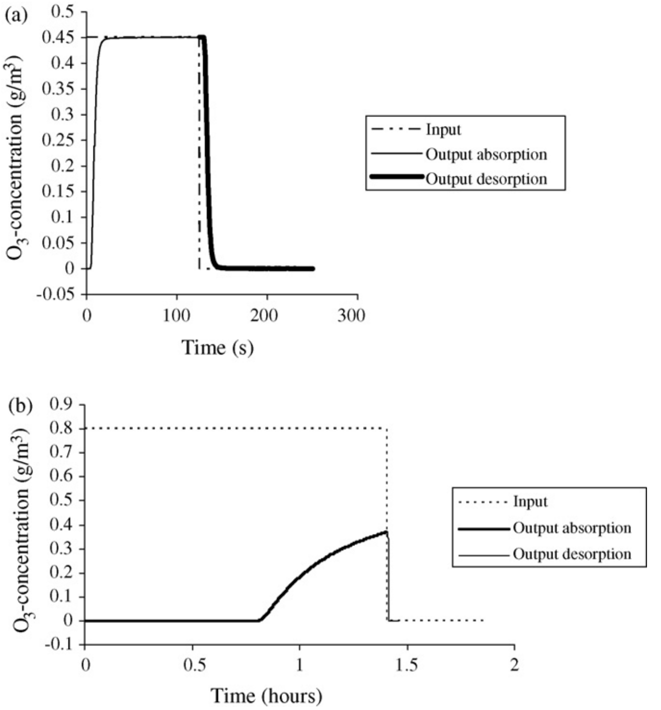

Fig. 2. Example of absorption/desorption profiles in case of no reaction present. (Teflon 65 N polymer, $T = 296.95$ K) (a) and in case reaction is present (HDPE polymer, $T = 293$ K) (b).

$$t_{\mathrm{total\ desorption}} = \int \left(\frac{C_{\mathrm{t}} - C_{\mathrm{t}=\infty}}{C_{\mathrm{t}=0} - C_{\mathrm{t}=\infty}}\right) \times \mathrm{d}t \tag{10}$$

These values lead to a calculated sorption value for absorption and for desorption using Eq. (7). If both values are not significantly different from each other, it can be concluded that the decomposition of ozone or reaction of ozone is negligible, because all the ozone sorbed during the absorption experiment is found back during the desorption experiment.

An example of what happens if the ozone reacts is given in Fig. 2b (HDPE polymer). The absorption experiment here was started at time zero. After about 1.4 h, the 4-way valve is switched again (although the absorption experiment is not finished). After switching the 4-way valve, the column outlet ozone concentration decreases to zero so fast that: $t_{\mathrm{total\ desorption}} < t_{\mathrm{total\ absorption}}$. This means that a lot of the ozone molecules which “disappeared” during the absorption experiment are not found back during the desorption experiment, what leads to the conclusion that they have reacted (with the polymer, with polymer additives, with molecules sorbed into the polymer or self-decomposition). In this case, no sorption coefficient can be determined, because reaction and sorption are both present.

2.3.2. *Calculation of the theoretical variance of the solubility for the simulation*

If $S = f(k_1, k_2, \ldots, k_n)$ with k_1 to k_n, the theoretical variance on S can be given by [16]:

$$\sigma^2(S) = \left[\left(\frac{\partial S}{\partial k_1}\right)^2 \times \sigma^2(k_1)\right] + \left[\left(\frac{\partial S}{\partial k_2}\right)^2 \times \sigma^2(k_2)\right] + \dots + \left[\left(\frac{\partial S}{\partial k_n}\right)^2 \times \sigma^2(k_n)\right] \quad (11)$$

The S value can be written here in function of 16 independent variables. The MAPLE 9.5 program is used to calculate the different derivatives from the S function to the different variables. The results are implemented in an Excel worksheet to provide a tool for theoretical standard deviation estimation for the simulation.

3. Results

3.1. Teflon 65 N polymer

The calculated S data are presented in Table 2. From absorption curves, an S value of 0.16 ± 0.07 (standard deviation) mole O_3/m^3 polymer per mole O_3/m^3 air ($T = 296.95$ K, $n = 2$) resulted; from desorption curves an S value of 0.088 ± 0.080 (standard deviation) was obtained ($T = 296.95$ K, $n = 3$). The high standard deviation for Teflon 65 N relative to the value reported is due to the fact the difference between the retention time t_R and the dead time t_M is small in these experiments. To the best of our knowledge, this is the first reported experimental data of ozone solubility in polymeric material.

3.2. 'Reaction exhausted' PDMS polymer

In the first experiments with PDMS, it was observed from the sorption profiles that a reaction was present. It was decided to expose the polymer in the column to a certain ozone concentration until the solubility values for absorption and desorption were not significantly different from each other. After several days of exposure, sorption and desorption profiles proved to become stable, suggesting that reactivity in the column was exhausted. The reaction could have been taken place between ozone and the polymer, products added to the polymer (cross linker), molecules sorbed into the polymer or a combination of them. In [23] the influence of ozone exposure on silicone membrane mass transfer, parameters in different chemical environments have been investigated. Therefore, we define the polymer after ozone exposure as "reaction exhausted" PDMS polymer.

The results for "reaction exhausted" PDMS are given in Table 2. S values range from 1.199 to 0.774 for temperatures in between 20 and 40 °C. The enthalpy change for sorption (ΔH_s) calculated with the Van't Hoff equation $\ln(S) = \ln(S_0) - (\Delta H_S/(R \times T))$ is equal to −11.05 ± 0.98 (standard deviation) kJ/mole. This value is lower than the value for ozone in water [24]: −34.7 kJ/mole.

3.3. Hyflon AD80

The results for ozone sorption into Hyflon AD80 are also shown in Table 2. It proves that this polymer has the highest sorption coefficient of the tested polymers. The mean value of all measured sorption coefficients in "reaction exhausted " PDMS at 20 °C is 1.082, where the mean value of Hyflon AD80 at 20 °C is 4.142. The ΔH_s value determined is equal to −17.24 ± 1.17 (standard deviation) kJ/mole. This value is lower than the value for ozone in water [24]: −34.7 kJ/mole and and higher than the value for ozone in 'reaction exhausted' PDMS (−11.05 ± 0.98 (standard deviation) kJ/mole) as reported above.

Table 2
Experimental results

Polymer	Flow rate (ml/s)	Temperature (K)	Absorption		Desorption	
			S (mole O_3/m^3 polymer per mole O_3/m^3 air)	Standard deviation on S	S (mole O_3/m^3 polymer per mole O_3/m^3 air)	Standard deviation on S
Teflon 65 N	6.84	296.95	0.158	0.071	0.088	0.080
PDMS	6.83	298.85	0.881	0.216	1.005	0.077
	7.77	300.35	0.936	0.188	0.991	0.177
	6.97	306.15	0.941	0.127	0.858	0.105
	7.92	306.15	0.894	0.169	0.855	0.182
	7.06	313.15	0.806	0.099	0.774	0.080
	8.05	313.15	0.849	0.159	0.779	0.213
	6.74	293.15	1.043	0.148	1.057	0.139
	7.68	293.15	1.199	0.222	1.027	0.151
Hyflon AD80	6.79	293.15	4.335	0.193	3.971	0.117
	6.04	293.15	–	–	4.121	0.188
	6.84	298.15	3.824	0.137	3.549	0.147
	6.08	298.15	3.722	0.179	3.607	0.232
	6.72	283.15	–	–	5.300	0.250
	5.93	283.15	–	–	5.188	0.206
	6.81	288.15	–	–	4.794	0.168
	6.00	288.15	–	–	4.957	0.239

The sorption of a certain penetrant in a polymer is influenced by the penetrant's condensability (expressed by its critical temperature) and by polymer-penetrant specific interactions. If the sorption of different penetrants in polymers is primarily determined by the penetrant's condensability, a relationship can be found between the sorption of these different penetrants in the polymer and the critical temperature of the penetrants. This is nicely illustrated in [17] and [21]. From a correlation as given in [21] for Hyflon AD80, a sorption value of 1.6 is deduced for ozone in Hyflon AD80 at 35 °C.

An extrapolation of the experimental data to 35 °C with the van '*t* Hoff equation gives an ozone sorption value in Hyflon AD80 of 2.95 (mol O_3/m^3 polymer on mol O_3/m^3 air). This value is about two times higher than the value that can be deduced from the correlation between sorption in Hyflon AD80 at infinite dilution and the critical temperature of the penetrant reported in [21]. This suggests that the sorption value of ozone in Hyflon AD80 is influenced by the penetrant/polymer specific interactions.

3.4. Potential and limitations of the developed method

Provided that the polymers show inertness to ozone reactivity and have appropriate particle size, the method developed here shows new perspectives to determine ozone sorption into numerous polymers. However, the quality of the results in terms of uncertainty on the S values is determined by the uncertainty of the different variables. In order to check the range of S values that can be measured with a reasonable standard deviation, a simulation was set up.

Typical values and standard deviations which were used to perform the simulation are given. The simulation results are presented in Fig. 3. In general, it proves that the simulation matches well with the experimentally observed percentage RSD values. It is observed that S should be at least 1.55 to get RSD lower than 10%.

It can be noticed that about 75% of the total variance on S comes from the variances on V_4 and t_{total} for low S values. Both the standard deviations of V_4 and t_{total} are highly influenced by the fact that the 4-way valve is switched manually. If the standard deviation on breakthrough time could be reduced, for example by an automation of the valve switching, this would have a great influence on the percentage RSD of the measurements. In Fig. 3, the results are presented from a simulation with a standard deviation for the breakthrough time equal to 0.05 s. Now, ozone sorption coefficients from 0.96 can be measured with a percentage RSD smaller than 10%. Another possibility to reduce the percentage RSD is the use of a longer column. In Fig. 3, a simulation is presented if the column length is increased from 0.5 to 1.5 m. Here sorption values above 0.65 can be measured with percentage RSD lower than 10% even if the valve is operated manually.

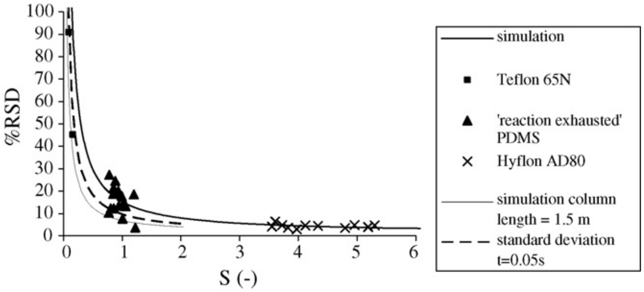

Fig. 3. Simulation of the expected percentage RSD based on typical values and standard deviations (full line); simulation with a reduced standard deviation to 0.05 s on the measurement of t_{total} (dotted line); simulation with a column length of 1.5 m (dashed line); experimental values.

4. Conclusions

A method to determine the solubility coefficient of ozone in different polymers was successfully developed. The particle size of the polymer applied is of major importance. To the best of our knowledge, we report for the first time ozone solubility data in polymeric materials. From the polymers tested, Hyflon AD80 ($S = 3.549 \pm 0.147$ mole O_3/m^3 polymer per mole O_3/m^3 air at $T = 298.15$ K, $n = 4$) has the highest solubility values, followed by "reaction exhausted PDMS" ($S = 1.005 \pm 0.077$ mole O_3/m^3 polymer per mole O_3/m^3 air at $T = 298.85$ K, $n = 5$). The value of Teflon 65 N was the lowest of the three polymers ($S = 0.088 \pm 0.080$ mole O_3/m^3 polymer per mole O_3/m^3 air at $T = 296.95$ K, $n = 3$).

$$\text{relative standard deviation (\%RSD)} = \frac{\text{standard deviation} \times 100}{\text{mean value}}$$

Acknowledgements

This work is supported by the BOF research fund (B/04929/01) from the Ghent University. Also the cooperation of Prof. P. van der Meeren (Particle and interfacial technology group (PaInT), Ghent university), Prof. F. Duprez and Dhr. Bernhard de Meyer (Department of organic chemistry, Ghent university), Prof. I. Van Driessche (Department of inorganic and physical chemistry, Ghent university) and the polymer suppliers (J. Van Dam (Dupont), G. Van Zandvoort (Helvoet), V. Everaert (Centexbel), P. Nagels (Solvay), L. Bernotti and C. Poli (Solvay Solexis), Prof. I. Vankelecom (university of Leuven) and Prof. G. Schoukens (Ghent university) is highly appreciated.

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