International Journal of Thermophysics, Vol. 26, No. 1, January 2005 (© 2005)
DOI: 10.1007/s10765-005-2357-z

Directs Measurement of High Temperature/High Pressure Solubility of Methane and Carbon Dioxide in Polyamide (PA-11) using a High-Pressure Microbalance[1]

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Experiments to determine the solubility of methane and carbon dioxide in PA-11 have been performed in the temperature range 50–90 °C and the pressure ranges 50–150 bar for methane and 20–40 bar for carbon dioxide. In general, the results agree fairly well with previous experiments for similar polymers, as well as showing correct trends in terms of temperature and pressure. The solubility of the gases follows Henry's law-type behavior except for methane at very high pressures. Diffusivities were also measured for the same systems at the same conditions. While the diffusivities are subject to more uncertainty than the solubility measurements, the expected (Arrhenius) trends are observed. Agreement with other experimental data using different methods is also good.

KEY WORDS: diffusivity; microbalance; polyamide; solubility.

1. INTRODUCTION

In part two of a program to measure gas solubility in three polymers used in flexible pipes used as flowlines and risers in the offshore oil and gas industry, we have completed measurements to determine the solubility of methane and carbon dioxide in polyamide (PA-11) in the temperature

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[1] Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22–27, 2003, Boulder, Colorado, U.S.A.

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range 50–90 °C. Measurements have been completed for the same gases in polyethylene in the temperature range 25–50 °C [1]. The temperature range at which the measurements take place is determined by the typical operating temperature of the polymer material in the pipe. Work is currently in progress to measure gas solubility in poly(vinylidene fluoride) in the temperature range 80–120 °C. The pressure ranges at which experiments were performed are 50–150 bar for methane and 20–40 bar for carbon dioxide.

2. MATERIALS

The PA-11 used in the study was supplied by NKT Flexibles. Samples were cut from extruded pipe intended for offshore use. The polymer contains 12–15% plasticizer. The sample used in this study had a measured plasticizer content of 14.5%. The reported density of the polymer was $1.05\,\mathrm{g\cdot cm^{-3}}$. The samples used in this study had a measured density of $1.06\,\mathrm{g\cdot cm^{-3}}$. The PA-11 was cut into small disks about 1 cm in diameter and 1 mm thick. Five disks were used in the experiments to give a polymer mass at the beginning of the study of 0.3168 g. A second, shorter, study was performed at the end of a complete cycle of experiments with a starting polymer mass of 0.2950 g. The mass of polymer was compensated by placing small quartz spheres on the opposite arm of the balance as described previously [1]. Methane and carbon dioxide gas samples were supplied in industrial gas bottles by Hede Nielsen, Denmark. The purity of the gas samples was better than 99.99%.

3. EXPERIMENTAL

The experimental apparatus and procedures have been described previously [1]. The heart of the process is a high-pressure balance Type S3D-P provided by Sartorius AG of Germany. The principle of the balance is straightforward. Gas is introduced into a high-pressure chamber where the polymer sample is being weighed. The mass of the sample increases as gas is dissolved into the polymer. When the mass of the sample and gas no longer increases (24 h is usually found to be more than enough time), the equilibrium solubility has been attained. The solubility of the gas is then simply

$$S = \frac{m_{\text{sample}}^{\text{new}} - m_{\text{sample}}^{\text{old}}}{m_{\text{sample}}^{\text{old}}}, \tag{1}$$

where the solubility (S) is in g(gas)/g(polymer) and the masses (m) are in g or mg. Solubilities can also be determined from the reverse experiment,

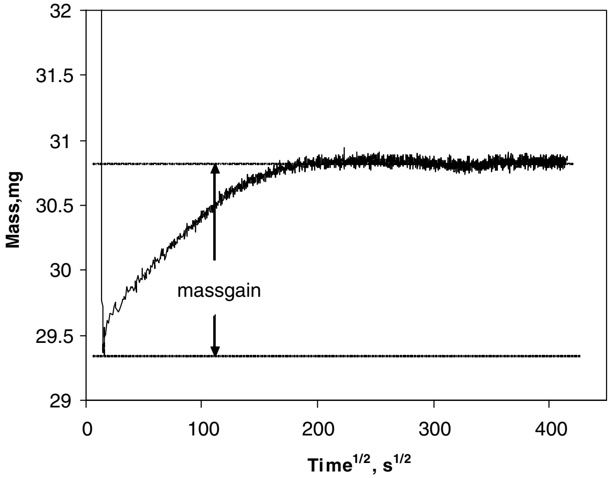

Fig. 1. Pressurization cycle for methane at 100 bar and 50 °C. The mass gain divided by the net polymer mass gives the solubility of the gas.

i.e., by measuring the mass reduction when a sample at equilibrium with a gas at pressure is evacuated. In this case, the mass loss determines the solubility of the gas in the polymer. Figure 1 illustrates the calculation of solubility for the pressurization cycle of methane at 100 bar and 50 °C. The mass gain is $(30.8 - 29.38) = 1.42\,\text{mg}$. The polymer mass at this point was 314.9 mg. So the solubility is 0.00451 g(gas)/g(polymer). Solubility is often reported as a solubility coefficient,

$$S_v = S \frac{\rho_{\text{polymer}}}{\rho_{\text{gas(STP)}} P}, \tag{2}$$

where S_v indicates a volumetric solubility coefficient in units of cm^3 $(\text{STP}) \cdot \text{cm}^{-3} \cdot \text{bar}^{-1}$, the densities ρ are in $\text{g} \cdot \text{cm}^{-3}$ and the pressure P is in bar. The densities of methane and carbon dioxide at STP are 0.7175 and $1.9777\,\text{kg} \cdot \text{m}^{-3}$ respectively. For the case of Fig. 1 we have $S_v = 0.062\text{cm}^3$ $(\text{STP}) \cdot \text{cm}^{-3} \cdot \text{bar}^{-1}$.

Table I shows the sequence of the experiments performed. Measurements were made at three temperatures for each gas/polymer pair, for a total of six experiments. Experiment 6 was then repeated with a fresh polymer sample. An experiment consists of pressurizing to three different pressures with evacuation occurring between pressurization runs. Thus, for example, experiment 1 consists of pressurizing the high-pressure chamber with methane at 50 bar, followed by evacuation to about 0.3 bar, followed by pressurization to 100 bar, etc. In this way, six solubility measurements

Table I. Experimental Program Sequence

Expt. no.	Gas	Temperature (°C)	Pressure (bar)			
1	CH_4	50	50	100	150	–
2	CO_2	50	20	30	20	40
3	CO_2	70	20	30	40	–
4	CH_4	70	50	100	150	–
5	CH_4	90	50	100	150	–
6	CO_2	90	20	30	40	–
7	CO_2	90	20	30	30	–

Experiment 7 was made with fresh polymer.

can be obtained at each temperature for each gas (i.e., for one experiment in Table I). At the end of a complete cycle of experiments (after experiment 6), the polymer sample was removed and weighed. It was found that the polymer mass had decreased from 0.3168 to 0.2834 g, a decrease of 10.5%. Since the polymer is known to contain 14.5% plasticizer, it is likely that this mass loss is due to the plasticizer being removed from the polymer during the course of the experiments. Furthermore, the polymer color had changed from a whitish grey to a pale yellow. Analysis of the polymer after the experiments revealed that it contained only 3.9% plasticizer—in agreement with measurements from the balance. The absolute mass of the polymer is not measured during the course of a run, rather, the solubility is calculated from the change in mass of the sample and a knowledge of the initial mass of the polymer at the beginning of the experimental cycle. However, the net (gas-free) mass of the polymer can be inferred during an experiment. Figure 2 shows the polymer mass vs. $t^{1/2}$ for the 100 bar pressurization and evacuation cycle of experiment 1 (methane at 50 °C). The differential mass (polymer sample minus quartz beads) in vacuum is 44.6 mg before pressurization to 100 bar begins. At the end of the evacuation cycle (before the next pressurization cycle to 150 bar), the mass is 42.9 mg. This loss of mass is assumed to be plasticizer that is removed during the evacuation cycle. An inspection of both the pressurization and evacuation cycles reveals that the mass is constant during pressurization, while dropping continuously during evacuation. Summing all these incremental mass losses throughout the first six experiments, it was calculated that the polymer mass should be reduced to 0.2858 g. This is in good agreement with the actual measured value of 0.2834 g. For most of the early runs, only the pressurization measurements were used in the determination of solubility. When evacuation measurements were used, the polymer mass was assumed to be the average of the mass at the start of pressurization and the mass at the end of the evacuation cycle. Thus, in

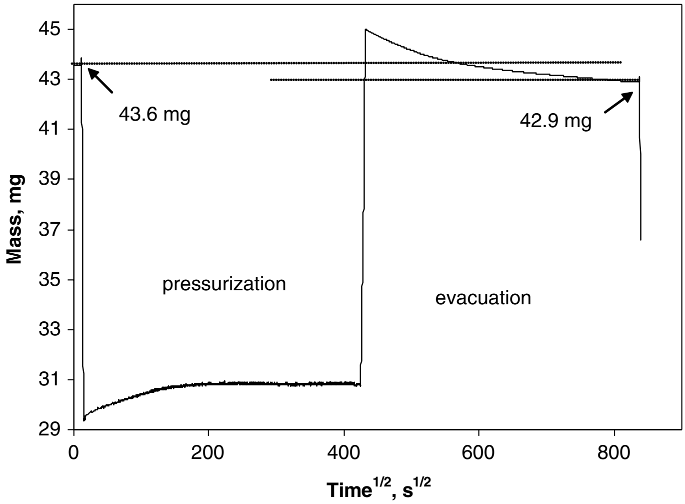

Fig. 2. Sequence of pressurization and evacuation runs for methane at 50 °C and 100 bar. Differential mass (polymer sample – quartz beads) in vacuum is 44.6 mg before pressurization to 100 bar begins. Mass in vacuum at the end of the evacuation cycle (before the next pressurization cycle to 150 bar) is 42.9 mg.

the example of Fig. 2, the starting mass was 314.9 mg and this is the value used in the calculation of solubility for the pressurization cycle. However, 0.7 mg of mass is lost during evacuation, so the polymer mass during evacuation is assumed to be the average of 314.9 and 314.2 mg (314.55 mg).

4. RESULTS AND DISCUSSION

Figures 3 and 4 show the results for methane and carbon dioxide solubility respectively, in PA-11. The individual determinations are shown in Tables II (methane) and III (carbon dioxide). The general trends are as expected, i.e., the solubility is linear in pressure at each temperature for both methane and carbon dioxide. However, the 150 bar results for methane at 50 and 70 °C show aberrant behavior. This may be partially explained as a deviation from Henry's law behavior—a phenomenon observed previously in high-density polyethylene—at least, for the result at 70 °C. The low value for the run at 50 °C and 150 bar might be explained by the fact that this was the first experiment in the series. Only one (pressurization) run was used to determine this point. It is possible that at this stage, when the polymer contained a large amount of plasticizer, the plasticizer was dissolving in the high-pressure methane, even as the methane was dissolving in the polymer, yielding a spuriously low value for the solubility (Table II).

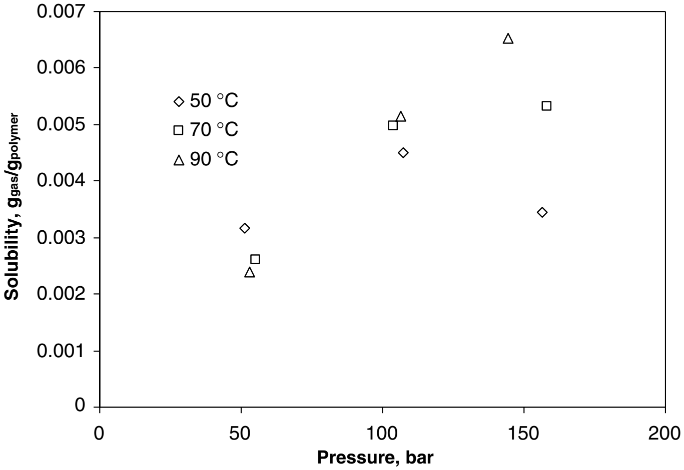

Fig. 3. Solubility of methane in PA-11 as a function of pressure at 50 °C (diamonds), 70 °C (squares), and 90 °C (triangles).

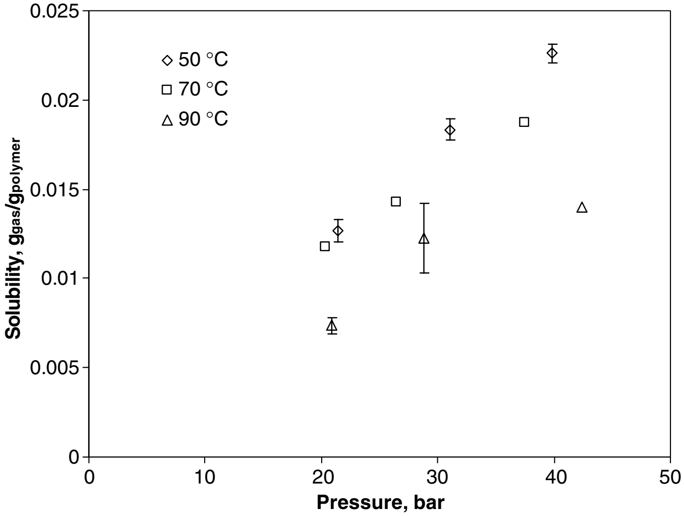

Fig. 4. Solubility of carbon dioxide in PA-11 as a function of pressure at 50 °C (diamonds), 70 °C (squares), and 90 °C (triangles).

Figures 5 and 6 show how solubility varies with temperature at constant pressure. The figures also show the results of Flaconnèche et al. [2] for the same systems. In Fig. 5, our study shows a higher solubility for methane in PA-11 than Flaconnèche et al. [2]. Neither work predicts a marked effect of temperature on solubility. The results for carbon

Table II. Solubilities of Methane in PA-11

$T = 50\,°C$		$T = 70\,°C$		$T = 90\,°C$	
Pressure (bar)	Solubility $\times 10^3$ (g gas/g polymer)	Pressure (bar)	Solubility $\times 10^3$ (g gas/g polymer)	Pressure (bar)	Solubility $\times 10^3$ (g gas/g polymer)
51.2	3.18	55.3	2.61	53.1	2.38
107.2	4.51	104.0	4.97	106.5	5.14
156.6	3.45	158.1	5.33	144.4	6.52

Pressure is either pressure applied during a pressurization run or equilibrium pressure immediately preceding an evacuation run.

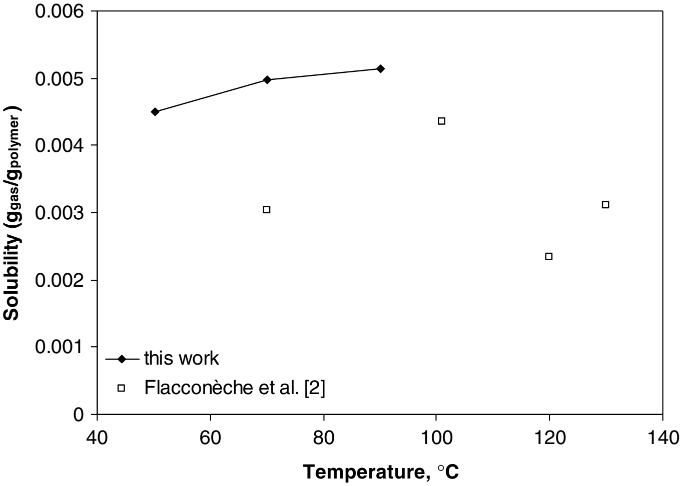

Fig. 5. Solubility of methane in PA-11 as a function of temperature at a constant pressure of 100 bar. Solid diamonds are the results of this work. Open squares are the data of Flaconnèche et al. [2]. The line is a guide to the eye.

dioxide (Fig. 6) are in better agreement, and both sets of data predict a drop in solubility with increasing temperature, as predicted by theory [3] (Table III).

Flaconnèche et al. [2] also studied the effect of plasticizer content on the solubility of various gases in PA-11. They found that the solubility was unchanged over a range of plasticizer content from 0 to 30%. The plasticizer used in that work was *n*-butyl-benzene sulfonamide. However, they did find that the permeability and diffusion were both strongly affected by plasticizer content, the permeability increasing by a factor of about five

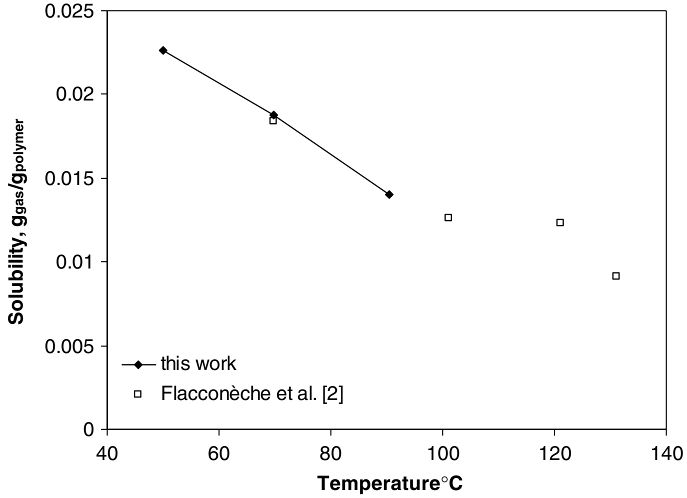

Fig. 6. Solubility of carbon dioxide in PA-11 as a function of temperature at a constant pressure of 40 bar. Solid diamonds are the results of this work. Open squares are the data of Flaconnèche et al. [2]. The line is a guide to the eye.

Table III. Solubilities of Carbon Dioxide in PA-11

$T = 50°C$		$T = 70°C$		$T = 90°C$	
Pressure (bar)	Solubility × 10^3 (g gas/g polymer)	Pressure (bar)	Solubility × 10^3 (g gas/g polymer)	Pressure (bar)	Solubility × 10^3 (g gas/g polymer)
22.1	12.8	20.3	11.8	20	6.93
21	13.4			21.8	7.82
21	11.8				
31.1	18.9	26.4	14.3	30.4	12.0
31.1	17.8			27.9	9.94
				28.2	14.8
39.8	23.1	37.5	18.7	42.4	14.0
39.8	22.1				

Pressure is either pressure applied during a pressurization run or equilibrium pressure immediately preceding an evacuation run.

as the plasticizer content was increased from 0 to 30% for both methane and carbon dioxide. This effect has been observed in this laboratory [4] in a 2-D permeation cell, where the permeability of PA-11 was drastically reduced following suspected removal of plasticizer, possibly from exposure to carbon dioxide at high pressures.

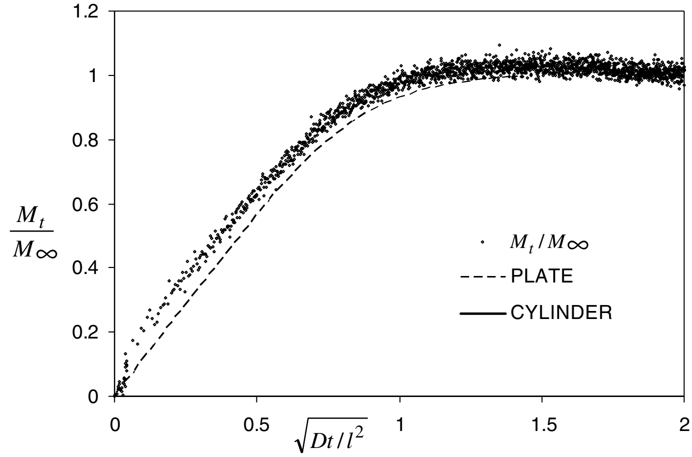

Fig. 7. Mass of gas dissolving in the polymer as a function of dimensionless time for methane at 50 °C and 100 bar. Solid line is the theoretical curve for a cylinder of diameter 0.88 cm and thickness 0.099 cm. (*l* is half the thickness of the polymer cylinder.) Dashed line is the theoretical curve for diffusion into a flat plate. Since the cylinders are disk-shaped, this is usually a good assumption and simplifies the calculations. Points are experimental measurements

The high-pressure balance can also be used to measure diffusivity of gases in polymers, as discussed previously [1]. Figure 7 shows the mass of methane dissolving in the polymer as a function of dimensionless time at 50 °C and 100 bar. The solid line is the theoretical curve for a cylinder of diameter 0.88 cm and thickness 0.099 cm (*l* is half the thickness of the polymer cylinder). The dashed line is the theoretical curve for diffusion into a flat plate. Since the cylinders are disk-shaped, this is usually a good assumption and simplifies the calculations. Points are experimental measurements. The full geometry of the cylinder was taken into account in estimating the diffusion coefficients, unlike in precious studies [1]. This was because the samples were thicker (the diameter-to-height ratio was lower). Figure 8 shows the results of the diffusivity determinations. The individual results are also tabulated in Tables IV (methane) and V (carbon dioxide). In general, the results are consistent and show good agreement with previous work [2]. The last experiment (experiment 7) was plotted separately for carbon dioxide in PA-11 at 90 °C. This was because this experiment was performed with a fresh sample of PA-11. It was estimated that the plasticizer content was about 3% in experiment 6, compared with 12% for the fresh polymer. Flaconnèche et al. [2] found that the diffusion coefficient increases with plasticizer content over a range from 0 to

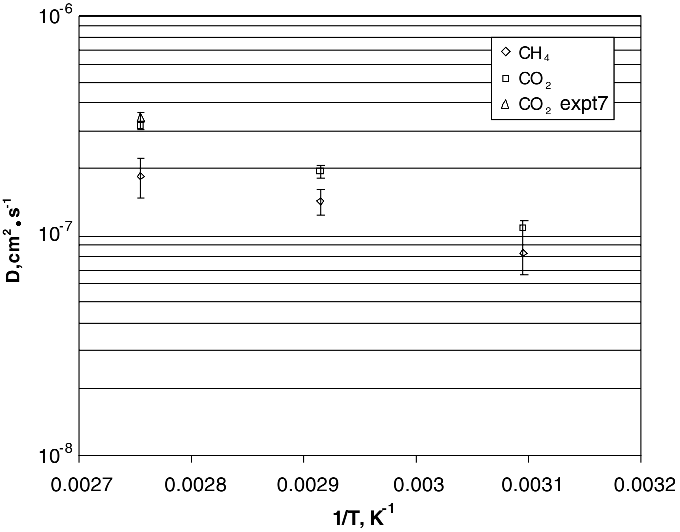

Fig. 8. Diffusivities of methane and carbon dioxide in PA-11 as a function of temperature. Values have been averaged over all the pressures at which measurements were made. Open diamonds are the values for methane and open squares for carbon dioxide. Open triangle is the value for experiment 7 with a fresh sample of PA-11.

Table IV. Diffusivities of Methane in PA-11

$T = 50°C$		$T = 70°C$		$T = 90°C$	
Pressure (bar)	Diffusivity $\times 10^7$ ($cm^2 \cdot s^{-1}$)	Pressure (bar)	Diffusivity $\times 10^7$ ($cm^2 \cdot s^{-1}$)	Pressure (bar)	Diffusivity $\times 10^7$ ($cm^2 \cdot s^{-1}$)
51.2	0.6	55.3	1.7	53.1	2.4
107.2	0.9	104.0	1.3	106.5	1.5
156.6	1.0	158.1	1.3	144.4	1.7

Pressure is either pressure applied during a pressurization run or equilibrium pressure immediately preceding an evacuation run.

30% plasticizer. In this study the diffusion coefficient increased from 3.2 to $3.5 \times 10^{-7} cm^2 \cdot s^{-1}$ for plasticizer contents of 3 and 12%, respectively. However, more experiments over a wider range of conditions need to be performed to establish the exact dependence of diffusivity on plasticizer content.

Table V. Diffusivities of Carbon Dioxide in PA-11

$T = 50\,^\circ\mathrm{C}$		$T = 70\,^\circ\mathrm{C}$		$T = 90\,^\circ\mathrm{C}$	
Pressure (bar)	Diffusivity $\times 10^7$ ($\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$)	Pressure (bar)	Diffusivity $\times 10^7$ ($\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$)	Pressure (bar)	Diffusivity $\times 10^7$ ($\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$)
22.1	1.0	20.3	1.8	20	3.1
21	1.0			21.8	3.5[a]
21	1.0				
31.1	1.2	26.4	2.1	30.4	3.0
31.1	1.1			27.9	3.3[a]
				28.2	3.6[a]
39.8	1.2	37.5	2.0	42.4	3.4
39.8	1.1				

Pressure is either pressure applied during a pressurization run or equilibrium pressure immediately preceding an evacuation run.

[a] Indicates fresh samples (samples from experiment 7) containing 12% plasticizer. It is estimated, based on the incremental mass loss of the polymer, that the samples used in experiment 6 contained about 3% plasticizer.

5. CONCLUSION

Experiments to determine the solubility and diffusivity of methane and carbon dioxide in PA-11 have been performed in the temperature range 50–90 °C and the pressure ranges 50–150 bar for methane and 20–40 bar for carbon dioxide. In general, the results agree fairly well with previous experiments, as well as showing the correct trends in terms of temperature and pressure. The effect of plasticizer and how it affects the results (since the mass and the density of the polymer change as plasticizer is removed) should be addressed. In addition, the effect of plasticizer removal from flexible pipes in place should be explored, both in terms of reduced permeability, which is desirable, but also in terms of the mechanical integrity of the pipes, which become more brittle, and may also shrink, compromising polymer/metal joints and fittings.

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