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Sorption of liquid propane in polyethylene

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Abstract

The kinetics of sorption and desorption of liquid propane in medium density polyethylene were studied by thermogravimetry as a function of temperature, pressure and time. Diffusion was mainly Fickian. Diffusion coefficients were of the order of 10^{-7} to 10^{-9} (cm^2 s^{-1}) and the Arrhenius temperature dependence was obeyed with an activation energy of 52.2 kJ mol^{-1} in the temperature range between 0°C and 70°C. At 0°C gradual plasticisation led to non-Fickian diffusion in the case of sorption. The saturation concentrations of propane were typically 8 to 10% by mass in the temperature range 0-40°C calculated from boundary conditions fitted to a diffusion model. The sorption of propane led to an initial increase in oxidative induction time on exposure most probably due to solvation of precipitated antioxidant by the sorbed propane.

1. INTRODUCTION

Polyethylene pipes dominate the market for propane and natural gas distribution systems operating at internal absolute pressures lower than 0.5 MPa. Figure 1 shows that propane is gaseous at the maximum pressure at temperatures above 0°C. However, there is always a possibility that the "ideal"

This paper was presented at the 13th Nordic Symposium on Thermal Analysis and Calorimetry, Stockholm, Sweden, 9–11 June 1992 condition will not prevail and that liquid propane is formed. Polyethylene pipes may also be used in distribution systems for liquid propane. Relatively little research have been performed on the effects of liquid propane on polyethylene [1, 2]. This paper deals with the kinetics of sorption of liquid propane in medium density polyethylene (MDPE) pipes and the interaction of the solvent with antioxidants present.

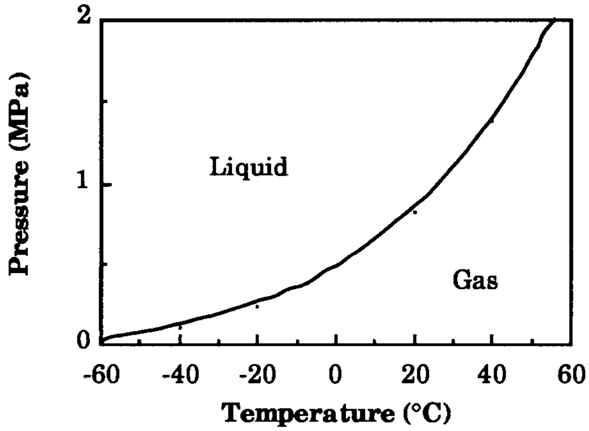

Figure 1. Gasol propan 95 phase diagram drawn after data in ref. [3].

Dos Santos et al [1] measured the permeation flux with liquid propane through membranes of low density polyethylene (LDPE) and found that the permeability reached a maximum at the condensation point. In an earlier paper [2], data were presented for the Flory-Huggins interaction parameter for gaseous propane and LDPE at pressures between 0.17 and 0.36 MPa. The interaction parameter, reported to be pressure-independent, increased with decreasing temperature to reach a constant value of 1.35 near the condensation point. It was suggested that the change in interaction parameter was due to a reduction in segmental mobility and cluster formation within the solvent, driven by the temperature decrease despite the potential plasticisation by the propane [2]. A strong activity dependence of the solubility coefficient (S) was observed for gaseous propane close to the condensation point (higher S values with higher activities). Mutter [4] studied sorption in MDPE pipes exposed to liquefied natural gas and observed a mass increase of more than 6% at 20°C.

2. EXPERIMENTAL

Pipes (12x1.8 mm) of a cadmium-pigmented branched polyethylene grade produced by Neste Polyeten AB, Sweden were exposed to liquid propane (gasol propan 95 with a propane content of 96 mol%) supplied by Statoil, Norway. C-13 NMR measurement showed that the polyethylene contained 0.5 mol% of ethyl branches. The density of the polymer was 939.6 kg m^{-3} corresponding to a volume crystallinity of 58% [5].

Sorption measurements were performed on 10±1 mg samples cut from the wall of pipes exposed to internal liquefied propane and external air-gaseous propane. The tests were performed at different constant internal absolute pressures between 0.47 MPa and 1.87 MPa at 0, 20 and 40°C for different periods of times up to almost 13 000 hours. The outer medium was held at atmospheric pressure by decompressing the autoclaves. The total amount of absorbed propane was obtained by thermogravimetry (TG) using a Perkin-Elmer TGS-2 measuring the mass loss in a heating scan from 35°C to 600°C at a rate of 20°C min^{-1} in He atmosphere.

The isothermal desorption measurements were performed by TG on propane-saturated sheet samples of thickness 150-240 μm under isothermal conditions from 30 to 70°C (atmospheric pressure, He atmosphere). The samples were originally exposed to liquid propane for several weeks. The diffusion coefficient (D) was calculated from the equation given in ref. [6]:

$$D = \left(\frac{\pi}{16}\right)\left(\frac{\partial\left(\frac{M_t}{M_\infty}\right)}{\partial\left(\frac{t^{0.5}}{l}\right)}\right)^2 \tag{1}$$

where M_t is the mass of desorbed propane at time t, M_∞ is the mass of desorbed propane after infinite time and l is the sample thickness. Supplementary isothermal desorption measurements were performed at three temperatures (0, 20 and 40°C) on samples cut from a pipe with 3.42 kg sorbate (100 kg $polymer)^{-1}$, the mass loss being recorded in a Mettler AE 163 balance with air as surrounding medium at atmospheric pressure. The diffusion coefficent values, considered constant, were derived from the time to reach 50% mass loss ($t_{0.5}$) assuming infinite sheet sample configuration [7]:

$$D = \frac{0.04919}{\left(\frac{t_{0.5}}{l^2}\right)} \tag{2}$$

Non-isothermal desorption experiments were performed in the TG apparatus by heating the sheet samples from 30 to 115°C at rates of 7 and 10°C min^{-1}. The other experimental conditions were the same as those of the isothermal desorption experiment. The mass loss data were then treated according to the procedure of Miller and Wildnauer [8] and the diffusion coefficient, assumed constant, was calculated from the equation:

$$\frac{-\partial\left(1-\frac{M_t}{M_\infty}\right)}{\partial t} = \left(\frac{8D}{l^2}\right)\sum_{n=0}^{\infty} e^{-(2n+1)^2\left(\frac{D\pi^2}{l^2}\right)t} \tag{3}$$

Oxidative induction time (OIT) measurements on 5.0±0.3 mg samples cut from the propane-exposed pipes were made between 155 and 215°C in an oxygen atmosphere in a temperature-calibrated Perkin-Elmer DSC-2. The purge gas flow was 50 ml min^{-1} and the induction time was obtained from the intersection of the isothermal base line with the tangent at 1 mW exothermal deviation from the scanning baseline.

3. THE EVALUATION OF SORPTION KINETICS DATA

It is assumed that the propane concentrations at the inner (r=a) and the outer walls (r=b) were constant at C_1 and C_2 respectively and that D was independent of propane concentration. The concentration profile for an infinitely long cylinder with an initial concentration of propane of zero in the pipe wall (C_0=0) can be expressed by [10]:

$$C(r,t) = \frac{C_1 \ln\left(\frac{b}{r}\right) + C_2 \ln\left(\frac{r}{a}\right)}{\ln\left(\frac{b}{a}\right)} - \pi \sum_{n=1}^{\infty} A_n U_0(r\alpha_n) e^{-D\alpha_n^2 t} \tag{4}$$

where

$$A_n = J_0(a\alpha_n)\frac{C_2 J_0(a\alpha_n) - C_1 J_0(b\alpha_n)}{J_0^2(a\alpha_n) - J_0^2(b\alpha_n)} \tag{5}$$

$$U_0(r\alpha_n) = J_0(r\alpha_n)Y_0(b\alpha_n) - J_0(b\alpha_n)Y_0(r\alpha_n) \tag{6}$$

J_0 and Y_0 are first and second kind Bessel functions of order zero. The α_n:s are the positive roots of :

$$U_0(a\alpha_n) = 0 \tag{7}$$

Observe also that:

$$U_0(b\alpha_n) = 0 \tag{8}$$

The mass of propane entering the wall at r=a and at time t per unit length is (according to Fick's first law of diffusion):

$$m_a = -2\pi a D\left(\frac{\partial C}{\partial r}\right)_{r=a} \quad (9)$$

The mass of propane leaving the wall at r=b ans at time t per unit length is:

$$m_b = -2\pi b D\left(\frac{\partial C}{\partial r}\right)_{r=b} \quad (10)$$

The accumulated mass of propane per unit length of pipe during a time period of t becomes:

$$M_t = \int_0^t (m_a - m_b)\,dt \quad (11)$$

To obtain the derivatives in eqs. (9) and (10), eq. (4) is first rewritten in the form:

$$C(r,t)=H(r)-T(r,t) \quad (12)$$

where T(r,t) is the series part of the right-hand-side. Differentiation with respect to r gives:

$$\frac{\partial C(r,t)}{\partial r} = \frac{\partial H(r)}{\partial r} - \frac{\partial T(r,t)}{\partial r} \quad (13)$$

When this equation is introduced into eq. (11), the H-terms disappear since:

$$b\left(\frac{\partial H}{\partial r}\right)_{r=b} - a\left(\frac{\partial H}{\partial r}\right)_{r=a} = 0 \quad (14)$$

with

$$\frac{\partial H}{\partial r} = \frac{\frac{C_2 - C_1}{r}}{\ln\left(\frac{b}{a}\right)} \quad (15)$$

The total amount of propane absorbed in the pipe wall then becomes:

$$M_t = 2\pi D\int_0^t \left(a\left(\frac{\partial T}{\partial r}\right)_{r=a} - b\left(\frac{\partial T}{\partial r}\right)_{r=b}\right)dt \quad (16)$$

where

$$\frac{\partial T}{\partial r} = \pi \sum_{n=1}^{\infty} A_n \alpha_n U_0'(r\alpha_n)\, e^{-D\alpha_n^2 t} \tag{17}$$

and

$$U_0'(r\alpha_n) = J_0'(r\alpha_n) Y_0(b\alpha_n) - J_0(b\alpha_n) Y_0'(r\alpha_n) \tag{18}$$

According to Carslaw and Jaeger [10]:

$$J_0(z)Y_0'(z) - Y_0(z)J_0'(z) = \frac{2}{\pi z} \tag{19}$$

Hence

$$U_0'(b\alpha_n) = -\frac{2}{\pi b\alpha_n} \tag{20}$$

Combination of eqs. (6), (7) and (19) for $z = a\alpha_n$ lead to:

$$U_0'(a\alpha_n) = -\frac{2}{\pi a\alpha_n} \frac{J_0(b\alpha_n)}{J_0(a\alpha_n)} \tag{21}$$

Insertion of eq. (17) in eq. (16) gives:

$$M_t = 2\pi^2 D \int_0^t \left(\sum_{n=1}^{\infty} \left(aU_0'(a\alpha_n) - bU_0'(b\alpha_n) \right) A_n \alpha_n e^{-D\alpha_n^2 t} \right) dt \tag{22}$$

which after combination with eqs. (20) and (21) and rearrangement yields:

$$M_t = 4\pi D \sum_{n=1}^{\infty} \left(\frac{C_2 J_0(a\alpha_n) - C_1 J_0(b\alpha_n)}{J_0(a\alpha_n) + J_0(b\alpha_n)} \right) \int_0^t e^{-D\alpha_n^2 t} dt \tag{23}$$

The mean concentration of propane in the pipe ($\overline{C}(t)$) can be calculated from the following expression:

$$\overline{C}(t) = \frac{M_t}{\pi \left(b^2 - a^2 \right)} \tag{24}$$

With eq. (23) integrated and inserted into eq. (24), $\overline{C}(t)$ becomes:

$$\overline{C}(t)=\frac{4}{b^2-a^2}\sum_{n=1}^{\infty}\frac{B_n}{\alpha_n^2}\left(1-e^{-D\alpha_n^2 t}\right) \tag{25}$$

where

$$B_n=\frac{C_2J_0(a\alpha_n)-C_1J_0(b\alpha_n)}{J_0(a\alpha_n)+J_0(b\alpha_n)} \tag{26}$$

The α_n values can be evaluated according to the following polynomial [11]

$$\alpha_n=\frac{1}{a}\left[\begin{array}{l}\dfrac{n\pi}{\rho-1}-\dfrac{\rho-1}{8\rho n\pi}+\left[\dfrac{100\left(\rho^3-1\right)}{3(8\rho)^3(\rho-1)}+\dfrac{1}{(8\rho)^2}\right]\dfrac{(\rho-1)^3}{(n\pi)^3}\\ +\left[-\dfrac{32(1073)\left(\rho^5-1\right)}{5(8\rho)^5(\rho-1)}+\dfrac{50\left(\rho^3-1\right)}{3\rho(8\rho)^3(\rho-1)}-\dfrac{2}{(8\rho)^3}\right]\dfrac{(\rho-1)^5}{(n\pi)^5}+\ldots,\end{array}\right] \tag{27}$$

where $\rho=b/a$.

J_0 values were extrapolated from tabulated data [12]. J_0 values of over twenty were calculated from [13]. An alternative way to obtain the roots of U_0 and the Bessel functions satisfying them were performed by Euler iteration. This method was however less suitable since it appeared to be very sensitive to the actual choice of initial values.

The mean concentration after infinite time is (since $\lim_{t\to\infty} T(r,t)=0$):

$$\overline{C}_\infty=\frac{4}{\left(b^2-a^2\right)}\sum_{n=1}^{\infty}\frac{B_n}{\alpha_n^2}=\frac{1}{\pi\left(b^2-a^2\right)}\int_0^{2\pi}d\theta\int_a^b rH(r)dr \tag{28}$$

which after integration gives:

$$\overline{C}_\infty=\frac{1}{\ln\left(\frac{b}{a}\right)}\left[\begin{array}{l}\left(C_1\ln(b)-C_2\ln(a)-\dfrac{C_2-C_1}{2}\right)\\ +\dfrac{(C_2-C_1)}{\left(b^2-a^2\right)}\left(b^2\ln(b)-a^2\ln(a)\right)\end{array}\right] \tag{29}$$

The mean concentration can now be written:

$$\overline{C}(t)=\overline{C}_\infty-\frac{4}{b^2-a^2}\sum_{n=1}^{\infty}\frac{B_n}{\alpha_n^2}e^{-D\alpha_n^2 t} \tag{30}$$

which converges faster than eq. (25). Because of approximation effects (rounding off the values of J_0 and α_n), eq. (25) describes the sorption best at short times, whereas eq. (30) is a better descriptor for the sorption at longer times. Either of these two equations could in principle be used in the fitting of the experimental data. The majority of the data were however derived from short time exposures and hence eq. (25) was selected. The concentration terms in eq. (25) have the unit: kg propane (100 kg polymer)$^{-1}$.

4. RESULTS AND DISCUSSION

Figure 2 presents the experimental sorption data together with data obtained by fitting equation (25). The effect of the hydrostatic pressure on the propane sorption was insignificant compared with the scatter in the experimental data. The observed pressure-independence is in agreement with earlier data by Dos Santos and Leitao [1]. Castro et al [14] report that the sorption of liquid n-pentane and n-hexane in polyethylene was not dependent on pressure at pressures lower than those used in this study.

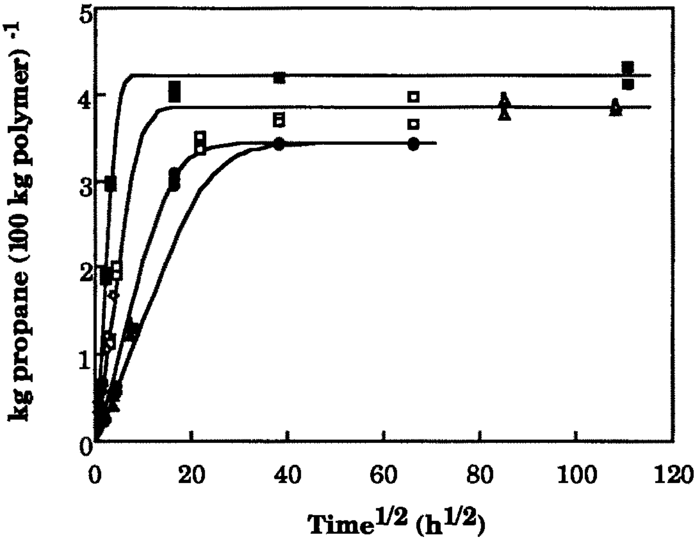

Figure 2. Sorption data obtained at different temperatures and different hydrostatic absolute pressures for internal liquefied propane and external air-gaseous propane: 0°C: ▲ 0.47 MPa, ● 1.39 MPa; 20°C: ◇ 0.83 MPa, □ 1.39 MPa, Δ 1.87 MPa; 40°C:■ 1.39 MPa. The solids lines are from best fits of eq. (25) at 1.39 MPa: 0°C: $D = 3.2 \times 10^{-9}$ cm^{2}s^{-1} (initial part), $D = 6.8 \times 10^{-9}$ cm^{2}s^{-1} (intermediate concentrations); 20°C: $D = 2.1 \times 10^{-8}$ cm^{2}s^{-1}; 40°C: $D = 8.6 \times 10^{-8}$ cm^{2}s^{-1}.

The fitting of eq. (25) to experimental data at 1.39 MPa absolute pressure was done by minimizing the sum of the squares of the differences (SSD) between experimental and predicted values. The adjustable parameters were D, C_1 and C_2. As a first step the range of possible outer boundary concentrations (C_2) were considered to be between 0 kg propane (100 kg polymer)$^{-1}$ and the equilibrium concentration in the polymer in contact with propane gas of 1 atm pressure.

Solubility data presented in ref. [2] were modified considering differences in crystallinity and were used to calculate the upper value of C_2. Eq. (29) then allowed upper and lower values of C_1 to be calculated. Stepwise and independent variation of the adjustable parameters C_1, C_2 (within upper and lower bound values) and D allowed the SSD to be minimized and eq. (25) to be fitted to the experimental data. The results of the fittings were as follows: 40°C: $D = 8.6\times10^{-8}$ cm^2s^{-1}, $C_1 = 9.6$ kg propane (100 kg polymer)$^{-1}$ and $C_2 = 0$ kg propane (100 kg polymer)$^{-1}$. 20°C: $D = 2.1\times10^{-8}$ cm^2s^{-1}, $C_1 = 8.5$ kg propane (100 kg polymer)$^{-1}$ and $C_2 = 0.2$ kg propane (100 kg polymer)$^{-1}$. The 0°C sigmoidal-shaped experimental curve could be described by an initial D value equal to 3.2×10^{-9} cm^2s^{-1} and a D value of 6.8×10^{-9} cm^2s^{-1} at intermediate propane concentrations, both having boundary conditions equal to 7.5 kg propane (100 kg polymer)$^{-1}$ on the inside and 0.2 kg propane (100 kg polymer)$^{-1}$ on the outside.

Figure 2 shows that the model describes well the experimental sorption data obtained at 20 and 40°C up to concentration levels equal to 60-80% of the saturation concentration. Sorption data obtained at 0°C deviated from Fickian behavior and could therefore not be described by only one diffusion coefficient.

The solubility data obtained for liquefied propane at 1.39 MPa exhibited an Arrhenius temperature dependence with an activation energy of 3.7 kJ mol^{-1} which was very different indeed from data of Michaels et al. [15] on gaseous propane and polyethylene showing a decreasing solubility with increasing temperature.

The diffusion coefficient values determined from the desorption data under isothermal and non-isothermal conditions applying equations (1-3) are presented in Figure 3 together with the diffusion coefficient data from the sorption measurements. The fit to the Arrhenius equation is good with a mean activation energy of 52.2 kJ mol^{-1} calculated from the data obtained by the four different methods: 51.4 kJ mol^{-1} (sorption data), 50.3 kJ mol^{-1} (isothermal desorption data, eq. (1)), 48.7 kJ mol^{-1} (isothermal desorption data, eq. (2)) and 58.3 kJ mol^{-1} (non-isothermal desorption data, eq. (3)). These data are in agreement with earlier data [16-18] on gaseous propane in the temperature range 5-60°C, varying between 50.0 and 56.9 kJ mol^{-1} and depending partly on the crystallinity of the polymer. The sorption and desorption diffusion coefficients are of the same order. At 0°C the initial sorption diffusion coefficient is lower than that obtained from desorption data (Figure 3) whereas the opposite relation is seen at intermediate concentrations indicating an anomalous diffusion [19]. The sum of the sorption diffusion and solubility activation energies, the activation energy of permeation, is 55.1 kJ mol^{-1} which is in agreement with earlier data [5].

The saturation concentration of propane , i.e. the concentration at the inner wall (C_1) was obtained from the fitting of eq. (25). The saturation concentration of propane in the amorphous component was temperature dependent and the following values were obtained considering that the volume crystallinity was 58%

and that the sorbate was confined to the amorphous component: 17.9% (w/w polymer) (0°C); 20.2% (w/w polymer) (20°C); 22.9% (w/w polymer) (40°C).

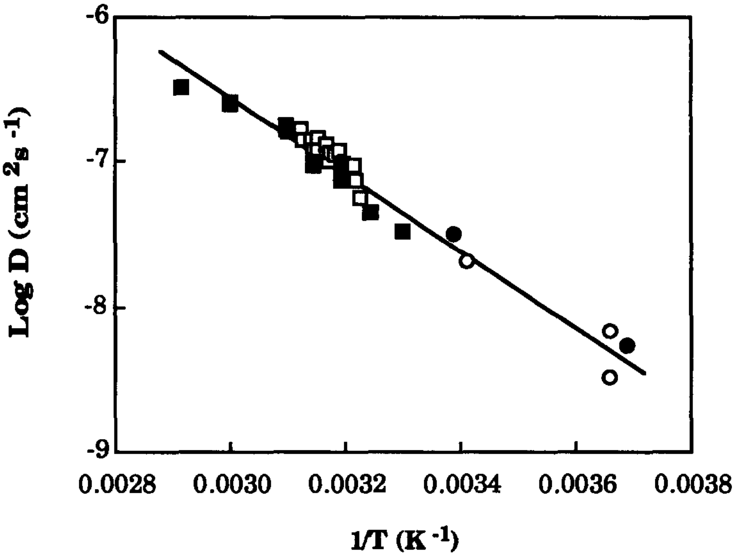

Figure 3. Arrhenius diagram of diffusion constant data: ○ sorption data; ■ isothermal desorption data (eq.(1)); ● isothermal desorption data (eq. (2)); □ non-isothermal desorption data.

The concentration of effective antioxidant was determined indirectly by OIT measurements and the results are shown in Figure 4. The antioxidant concentration in the unexposed pipe was set to 100% and changes with reference to this level of stabilization are given in Figure 4. The data for the same pipe exposed to internal water and external air exhibited the "expected" behaviour with a significant loss of antioxidant on exposure. It has been shown in earlier work [20,21] that the loss of the antioxidant is initially due to micro-blooming and early precipitation of the antioxidant of the super-saturated solution and later due to migration according to Fickian laws of the antioxidant to the surrounding media. The apparent increase in stability of the pipe exposed to liquid propane was indeed unexpected but may be due to solvation of precipitated antioxidant of the absorbed propane. It seems likely that propane is a better solvent for the antioxidant than polyethylene. The most marked solvation effect was observed at 40°C.

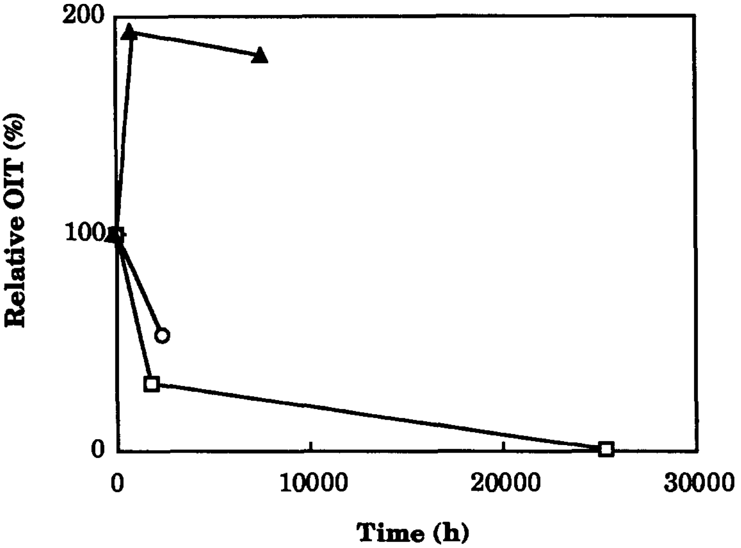

Figure 4. Relative OIT (mean value through the pipe wall cross-section) as a function of exposure time (t): ▲ liquefied propane (internal)/air (external) at 40°C; ○ water (internal)/air (external) at 80°C; □ water (internal)/water (external) at 80°C.

Homogenisation of antioxidants was also confirmed by the reduction in scatter of OIT data for the exposed pipes (relative standard deviation = 21%) compared with that for the unexposed pipes (relative standard deviation = 41%).

On prolonged propane exposure the antioxidant concentration decreased with increasing exposure time (Figure 4). This was particularly pronounced for the near-inner-wall material. The migration of the antioxidant was thus primarily directed towards the inner wall.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

1 D. M. Leitao and M. L. Dos Santos, J. Polym. Sci., Polym. Phys. Ed., 10 (1972) 1.
2 M. S. Dos Santos and D. M. Leitao, J. Polym. Sci., Polym. Phys. Ed., 10 (1971) 769.
3 Gasol Propan 95, product information paper, Statoil, Norway.
4 F. Mutter, Proc. Fifth AGA Plastic Pipe Symp. Houston, 1974, 2.
5 T. Tränkner and U. W. Gedde, Proc. 12:th A.G.A. Plastic Fuel Gas Pipe Symp., San Fransisco, 1991.
6 J. Crank, The Mathematics of Diffusion (2:nd ed.), Clarendon Press, Oxford, 1986, 244.
7 G. S. Park and J. Crank, Diffusion in polymers, Academic Press, New York, 1968, 16.
8 D. L. Miller and R. Wildnauer, Thermochim. Acta, 14 (1976) 151.
9 J. Crank, The Mathematics of Diffusion (2:nd ed.), Clarendon Press, Oxford, 1986, 84.
10 H. S. Carslaw and J. C. Jaeger, Conduction of heat in solids (2:nd ed.), Clarendon Press, Oxford, 1959, App. III.
11 R. M. Barrer, Diffusion in and through solids, University Press, Cambridge, 1951, 36.
12 A. Gray, G. B. Mathews and T. M. MacRobert, A Treatise on Bessel Functions, McMillan, London, 1931, 267.
13 S. M. Selby, Standard mathematical tables (24:th ed.), Ed. W. H. Beyer, CRC Press, Cleveland, 1976, 445-446 (eq. 5 and 6).
14 E. F. Castro, M. S. Vicente, E. E. Gonzo and J. C. Gottifredi, Latin Amer. Appl. Res., 18 (1988) 87.
15 A. S. Michaels and H. J. Bixler, J. Polymer Sci., 50 (1961) 393.
16 R. W. Macdonald and R. Y. M. Huang, J. Appl. Polym. Sci., 26 (1981) 2239.
17 H. Tschamler and D. Rudorfer, Mitteilungen Ósterreich. Kunststoffinst., 27 (1973) 25.
18 S. Pauly, Polymer Handbook (3:rd ed.), Eds. J. Brandrup and E. H. Immergut, Wiley , New York, 1989, VI-437.
19 J. Crank, The Mathematics of Diffusion (2:nd ed.), Clarendon Press, Oxford, 1986, 255.
20 K. Karlsson, G. D. Smith and U. W. Gedde, Polym. Eng. Sci., 32 (1992) 649.
21 G. D. Smith, K. Karlsson and U. W. Gedde, Polym. Eng. Sci., 32 (1992) 658.