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# Diffusivity of multicomponent gas mixtures in polyethylene

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**Abstract**

## 1. Introduction

The gas phase polymerization of ethylene to make polyethylene is the most widely exploited chemical reaction in the world in terms of annual volume of production. As such, the modelling of this process has attracted a significant investment of energy in the development of reactor models[1] and models of growing polymer/catalyst particles.[2,3,4] However, one significant point that emerges from a perusal of the references in the review articles just cited is that there is a significant lack of data concerning both solubility and diffusivity of multicomponent gas phase mixtures.[5,6,7,8] This information is crucial, particularly in terms of understanding mass transfer and the evolution of the concentrations of reactive species in the growing polymer particles under realistic polymerization conditions. Typical polymerization recipes contain not only ethylene, hydrogen, and nitrogen, but also comonomers and inert alkanes that help to improve the control of the reactor temperature by increasing the heat capacity of the gas phase, and, when liquefied, through the latent heat of evaporation. Alkanes are chemically inert but can nevertheless have a significant impact on the polymerization proves by modifying the nature of the amorphous phase of the polymer, and thus processes such as absorption and diffusion. The same is true of alkenes that are used as reactive comonomers. N.B. when alkanes are used to control the reactor temperature, they are often referred as induced condensing agents, ICA. In the current paper, we will refer collectively to all penetrants heavier than ethylene as ICA since alkanes and alkenes both have similar effects on ethylene (and each other).

The simultaneous sorption of multiple species (i.e., what really happens in an ethylene polymerization reactor) can change the way that each of them interact with the amorphous phase of the polymer. Heavier species (e.g., butane or pentane) can increase the solubility of lighter ones, in particular ethylene, and alter the diffusivities of the penetrants in the system. It has been shown in the literature[9,10] that accounting for the co-solubility and co-diffusivity effects can help to explain observed increases in productivity. Also, considering the interactions between the different species when calculating the diffusion coefficients improves the capacity of single particle models to explain high initial rates of ethylene polymerization in the presence of alkanes[9].

However, as mentioned above, diffusion and sorption data for multicomponent systems is sorely lacking. In one of the rare two penetrant systems studied in the literature, Cancelas et al.[11] studied the overall diffusivity of mixtures of ethylene and propylene in high impact polypropylene (hiPP) using a magnetic suspension balance (MSB) at temperatures between 50-85°C. They showed that the diffusivity of the ternary mixture is higher than the diffusivity of the pure components. In terms of diffusion in PE, Alves et al.[7] studied the diffusion of ethylene/n-hexane/PE and ethylene/n-pentane/PE by employing the free volume theory of Vrentas and Duda. They showed that, as expected, the ternary diffusivity of ethylene in presence of a heavier species is higher than its binary diffusivity due to the co-solubility effect increasing ethylene concentration in the amorphous phase of the polymer. They also showed that the ternary diffusivity of these alkanes increases compared to the binary one, which is not an expected result due to the anti-solvent effect of ethylene on ICA, decreasing ICA concentration in the amorphous phase of the polymer.

Clearly, it is desirable to be able to integrate such information into process models in order to help us better understand the impact of the process conditions on the final polymer product. It is therefore crucial to have more experimental and theoretical studies about the diffusion of mixtures of penetrants in the amorphous phase of the polymer since it has a great importance in ethylene polymerization reaction in gas phase.

In the current paper we will present an experimental study of the binary (one penetrant + linear low density polyethylene - LLDPE), ternary and quaternary diffusion of ethylene with propane, i-butane, and 1-butene. The overall diffusivity of ternary systems ethylene/propane/LLDPE, ethylene/isobutane/LLDPE and ethylene/1-butene/LLDPE at 70°C will be studied and compared to the binary ethylene/LLDPE system. Then, the quaternary overall diffusivity of ethylene/propane/1-butene/LLDPE and ethylene/isobutane/1-butene/LLDPE will be

investigated at 70°C and compared to ternary diffusivity. To the best of our knowledge, this is the first time that the diffusivity is investigated for such ternary and quaternary systems.

## 2. Estimation of diffusion coefficients

Sorption experiments with a magnetic suspension balance (MSB) can be used to measure both the equilibrium solubility and the overall diffusivity of a gas (or mixture of gases[6,11,12,13]). A typical sorption curve is shown in Figure 1. The equilibrium solubility of the penetrant(s) can be obtained from the steady state value of mass uptake, and an overall diffusion coefficient can be extracted from the rate of mass uptake in the dynamic part of the experiment.

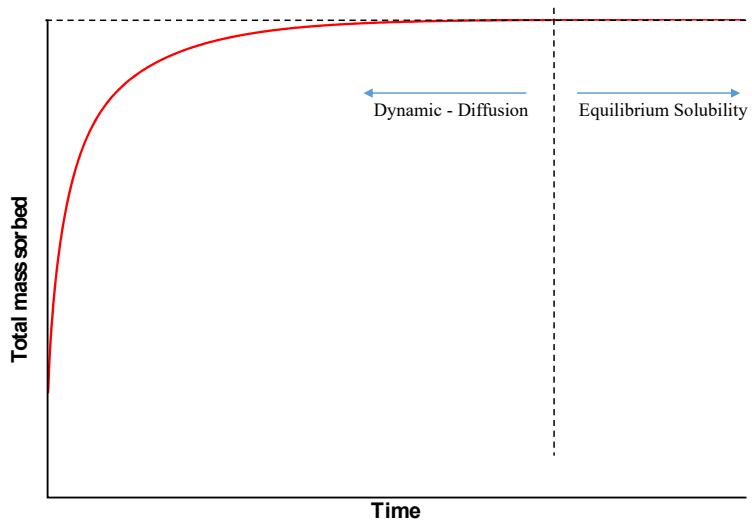


Figure 1. Example of sorbed mass uptake measured with a magnetic suspension balance.

If sorption takes place in spherical particles, one way of interpreting the transient portion of the sorption curve would be to use Crank's solution to the dynamic form of Fick's law for a spatially uniform sphere[14]:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-Dn^2\pi^2\frac{t}{r^2}\right) \quad (1)$$

Where $M_t$ is the mass sorbed at a given time $t$, $M_\infty$ is the total mass sorbed at equilibrium, $D$ is the diffusivity of the penetrant that is assumed independent of the concentration, and $r$ is the average radius of the polymer powders. From an experimental point of view, this means that if

we know *r*, we can use the sorption experiments to calculate an observed diffusivity for the system of interest, and vice versa.

Bobak et al.[15] and Zubov et al.[16] showed that one cannot use this approach for porous reactor particles of polyolefins because a single value of *D* and of *r* were not capable of predicting the shape of the degassing curves. While Zubov et al.[16] showed that transport resistance through the pores of particles during degassing experiments can be neglected they found that the diffusion coefficient that fits the first few seconds of the process appeared to be greater than that observed for the second part of the uptake curve. They attributed this to the fact that real polymer particles are not morphologically homogeneous, but rather are agglomerates of smaller granules having different sizes (and thus different values of *r*). They approximated the particle morphology by an agglomeration of compact polymer granules with 2 distinct sizes; one with a small radius and one with a larger radius to better fit the experimental mass uptake curves. The authors also stated that while this concept gives satisfactory results in terms of predicting experimental degassing rates, a real particle is in fact an agglomeration of many domains of different sizes. This seems reasonable as the polymer powder certainly has different lengths scales for diffusion, due to different particle sizes as well as different morphologies within each particle. These scales are more likely to be represented by a distribution rather than only two length scales. If we take this concept and assume that the distribution of substructure sizes with a distribution of characteristic radii, $w_i$, then equation (2) can be extended to:

$$\frac{M_\mathrm{t}}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{i=1}^{\infty}\sum_{n=1}^{\infty} w_i \frac{1}{n^2}\exp\left(-Dn^2\pi^2\frac{t}{r_i^2}\right) \tag{2}$$

where $w_i$ is the fraction of characteristic length scales with radius $r_i$. If these lengths are normally distributed, then the distribution can be written:

$$w_i = \frac{1}{\sigma\sqrt{2\pi}}\mathrm{e}^{-\frac{(r_i - r_\mathrm{m})^2}{2\sigma^2}} \tag{3}$$

where $\sigma$ is the standard deviation and $r_\mathrm{m}$ is the mean length scale. The advantage of using this approach is that one only needs to estimate an average mean size and a standard deviation rather than 2 radii and a weight fraction. With knowledge of the distribution $w_i$ it this possible to estimate the overall diffusivity *D*, or conversely if one has a reliable value for *D* it should be possible to estimate the parameters $\sigma$ and $r_\mathrm{m}$. In the following we will use known values of the

diffusivity of pure ethylene in LLDPE to estimate the average substructure size and the standard deviation for an LLDPE powder. This same powder will then be used in sorption experiments to determine the overall diffusivities of mixtures of ethylene and common process gases in LLDPE.

## 3. Experimental

A magnetic suspension balance (MSB) was used to measure the overall diffusivity of the different gas mixtures in PE. The configuration and operating mode for this MSB are presented elsewhere.[11,12] All sorption measurements were made using the same LLDPE powder. This raw reactor powder had not been granulated and was supplied by an industrial partner from their pilot plant site. It had a crystallinity of 48.3 % (w/w), a weight average molecular weight of approximately 152 kDaltons, and a polydispersity index of 8.8.

Scanning electron microscopic images of the LLDPE powder are shown in Figure 2 (a-c), and the particle size distribution (PSD) is shown in Figure 2 (d). It can be seen here that the PSD has two peaks, the majority peak centered on 500 μm, and a smaller peak at around 60 μm. Furthermore, examination of Figure 2 (a-c) shows that the particles are not spherical, but rather irregularly shaped, and that the larger particles have lobes, or substructures of various sizes and show a certain amount of macroporosity. As a precise estimate of the porosity of powder structures such as these is very difficult to obtain (it is almost impossible to differentiate between the internal macropores, and the interstices with such irregularly shaped objects), a value for this quantity cannot be provided. Nevertheless, visual inspection of the particles strongly suggests that using a distribution of substructures composed mostly of polymer to describe the morphology (as suggested above) is not at all unreasonable.

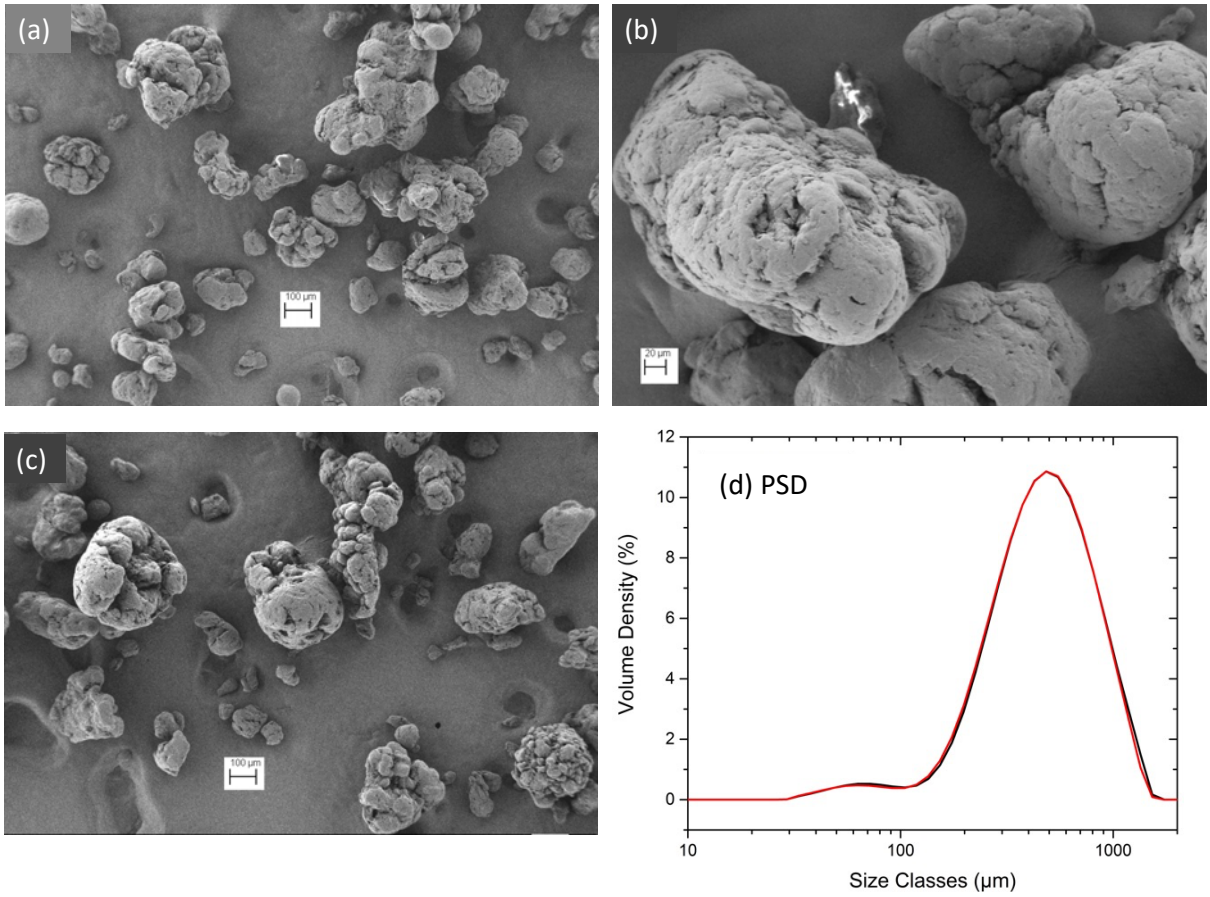


Figure 2. (a, b, c) SEM images of the LLDPE powder used in the work (50 X magnification) and (d) Particle size distribution.

## 4. Results and discussion

### 4.1 Estimation of distribution parameters

Obviously one can use equations (2) and (3) to estimate the diffusivity of a gas (mixture) if the size distribution of the substructures is known. However, if one knows the diffusivity in question, then the sorption experiments can be used to solve the inverse problem using the sorption curves to estimate the parameters of the substructural size distribution. In this case we used the model and parameters of Alves et al.[7] to calculated the diffusivity of ethylene in LLDPE. Their diffusivity values of ethylene in LLDPE should be comparable to those of the LLDPE powders used here as the they used a polymer with a crystallinity of 48.6 % for Alves et al.[1] The values used in the present work are shown in Table 1.

Table 1. Diffusivity data were taken from Alves et al. [7] at 70°C.

| P (bar) | 3 | 4.3 | 6.1 | 10.3 | 13.94 | 15 |
|---|---|---|---|---|---|---|
| $D$ (m$^2$ s$^{-1}$) | $4 \times 10^{-11}$ | $7.71 \times 10^{-11}$ | $1.02 \times 10^{-10}$ | $1.22 \times 10^{-10}$ | $1.58 \times 10^{-10}$ | $1.6 \times 10^{-10}$ |

The experimental sorbed weight were therefore fitted to Crank's diffusion equation to estimate the average size of particles, $r_{\mathrm{m}}$, and the standard deviation, σ, in equation (3). The fitting procedure minimizes the percent average relative deviation between the experiments and Crank's diffusion model:

$$J = \sum_{t=0}^{50\ \mathrm{s}} \left| \bar{M}_{\mathrm{t}}^{\mathrm{model}} - \bar{M}_{\mathrm{t}}^{\mathrm{exp}} \right| \tag{4}$$

where $\bar{M}$ stands for the normalized mass. Fitting was done over the first 50 seconds of the experiment, where a bigger variation of the absorption is observed.

Several experiments were used to estimate the values of $\sigma$ and $r_{\mathrm{m}}$ from sorption curves of ethylene in LLDPE. The results of these estimates are shown in Figure 3. Based on this we chose $r_{\mathrm{m}} = 160$ µm, and $\sigma = 98$ µm for all the of subsequent estimates.

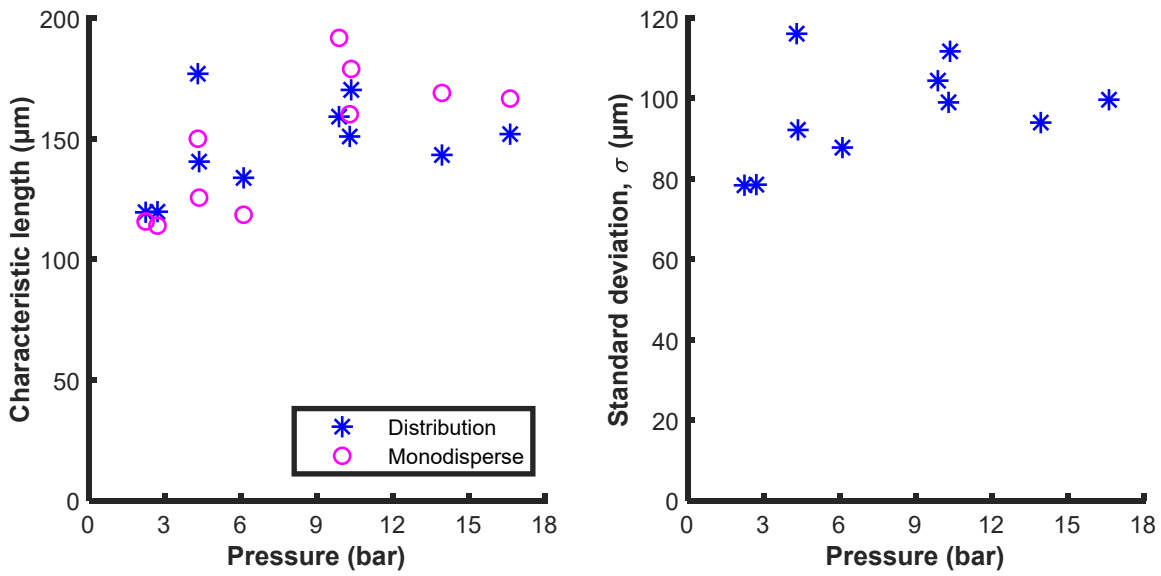


Figure 3. Estimation of the mean characteristic length, $r_{\mathrm{m}}$, and standard deviation, $\sigma$, of the used LLDPE particles from binary experiments

The results of 4 pure ethylene sorption experiments are shown in Figure 4 for a range of pressures, along with the model fits using the diffusivities in Table 1 and the distribution

parameters defined above. Note that the low-pressure experiments are noisier because of the moderate solubility of ethylene in the polymer, and the fact that the MSB can be influenced by vibrations in the laboratory. This led to a higher disparity in the estimated values of the diffusion coefficient at low pressures in Figure 3. Despite the experimental noise, a clear increase in the diffusivity can be observed at higher pressure.

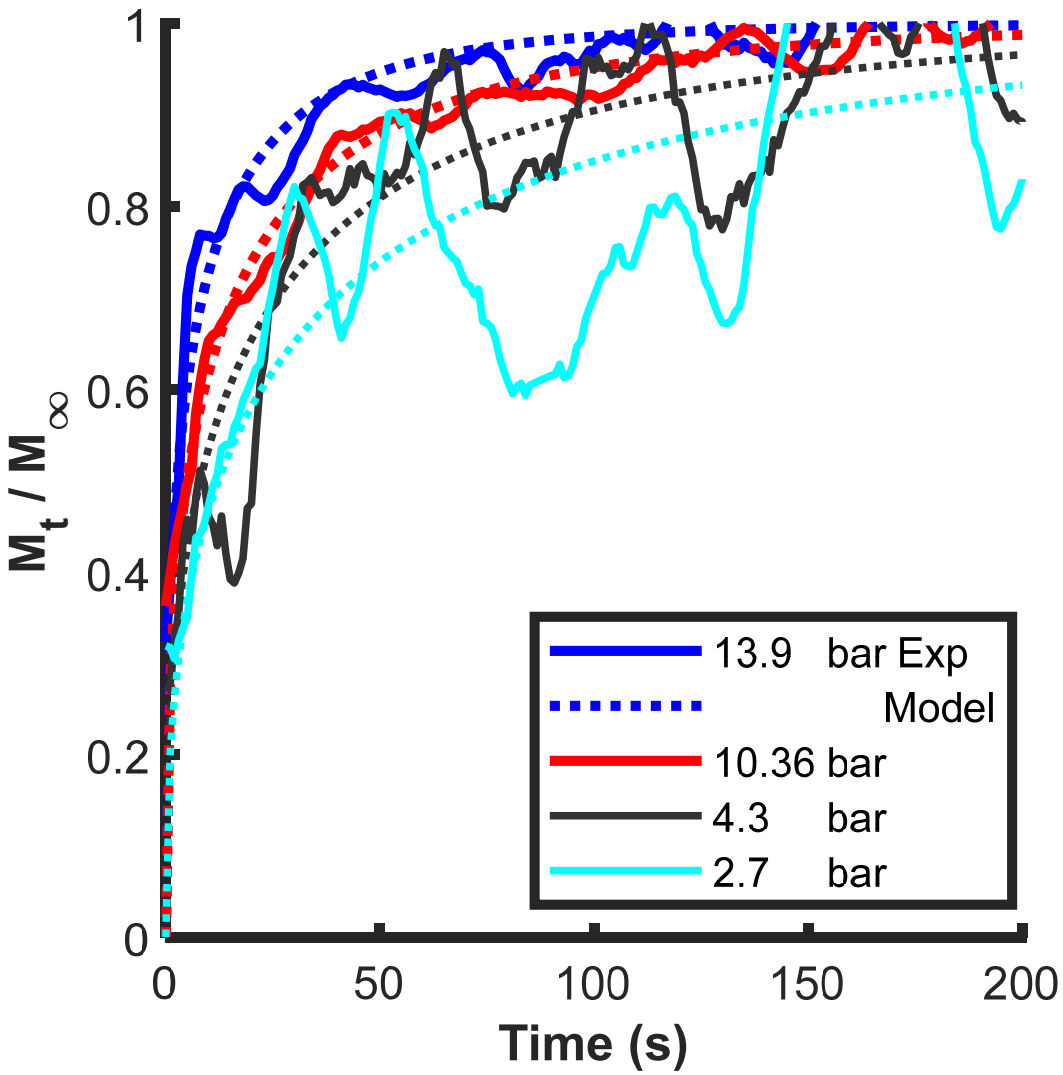


Figure 4. Sorption experiments for ethylene at pressures of 2.7, 4.3, 10.3 and 13.9 bars (solid lines) and model fits using the distribution in equation 3.

### 4.2 Estimation of diffusivity in higher order systems

The ternary systems of ethylene in LLDPE-B with different penetrants such as propane, isobutane and 1-butene were studied in this section. In this case, criterion 4 was minimized to identify $D$, by fixing $r_{\mathrm{m}}$ and $\sigma$. The overall diffusivity of these three systems were measured for a total pressure up to 5 bars and a constant temperature of 70°C. The gas phase composition of the different ternary systems considered in this section is presented in Table 2. It should be mentioned here that an effort was made to run the systems with the same fractions of ethylene and the co-sorbent, but as the feeds of the two gases needed to be adjusted by hand, there were variations from run to run. Figure 5 through Figure 7 show the normalized mass uptake curves, and the fit of the curve to determine the different diffusivities. The values of the diffusivities thus calculated are shown in Table 2 and compared in Figure 8.

***Table 2. Ternary systems at 70°C: Gas-phase molar composition, operating pressures, overall estimated diffusion coefficients. Ethylene (C2), propane (C3), isobutane (iC4), 1-butene (1C4).***

| System | Molar composition | Total pressure (bar) | D ($m^2\ s^{-1}$)× $10^{10}$ |
|---|---|---|---|
| **$C_2$/ C3/ LLDPE** | $x_{C2}$ = 0.509<br>$x_{C3}$ = 0.491 | 2.593 | 1.86 |
| | | 3.082 | 2.15 |
| | | 3.753 | 2.96 |
| | | 5.055 | 4.01 |
| **$C_2$/ iC4/ LLDPE** | $x_{C2}$ = 0.485<br>$x_{iC4}$ = 0.515 | 2.857 | 0.76 |
| | | 5.067 | 0.965 |
| **$C_2$/1C4/ LLDPE** | $x_{C2}$ = 0.617<br>$x_{1C4}$ = 0.383 | 2.6 | 1.08 |
| | | 3.927 | 2.11 |

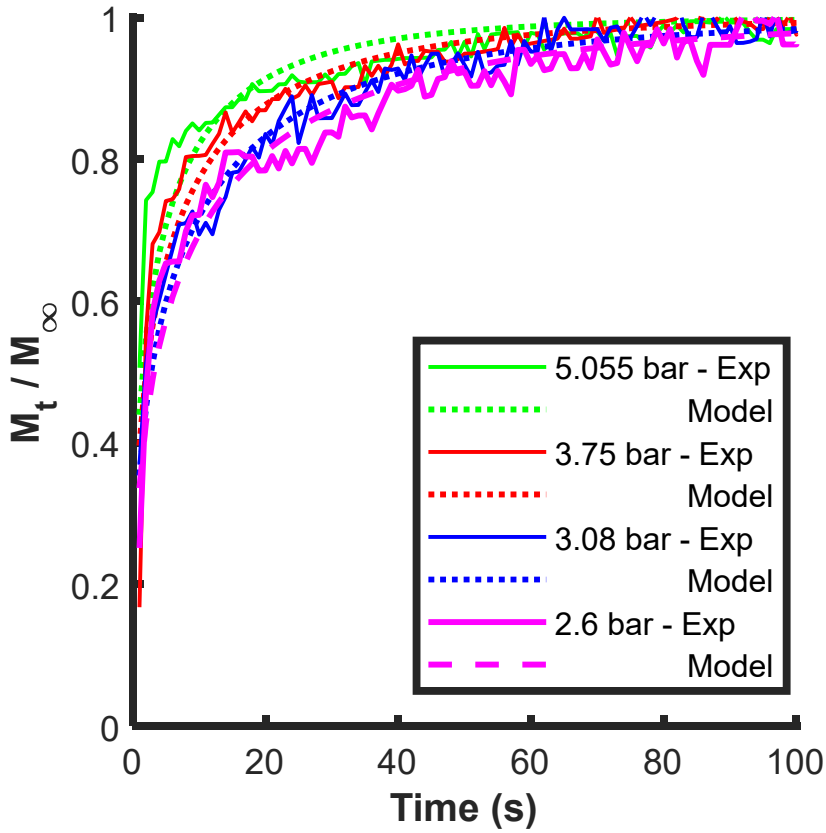


Figure 5. Fitting results of the ternary system $C_2$/ C3/ LLDPE at 70°C

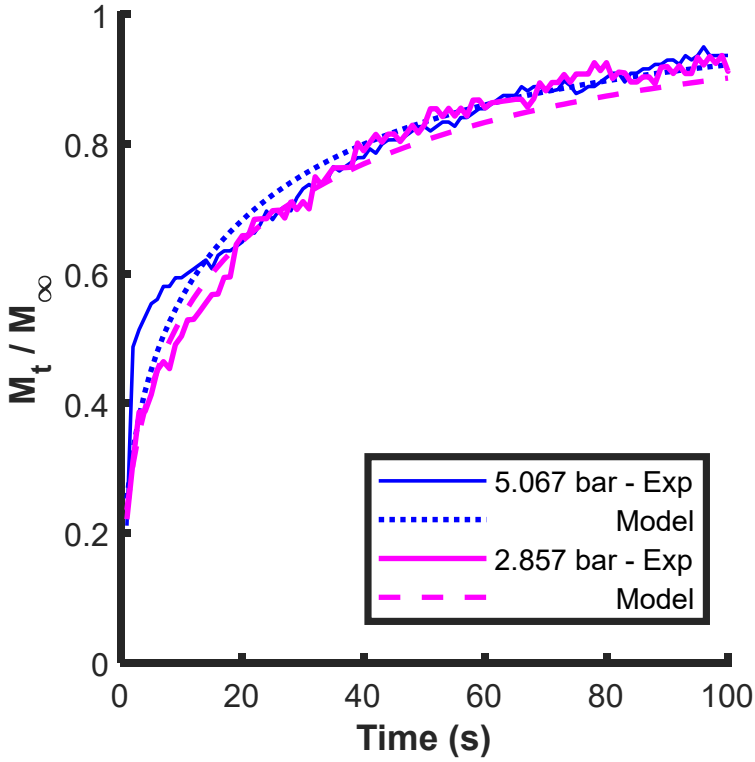


Figure 6. Fitting results of the ternary system $C_2$/ iC4/ LLDPE at 70°C

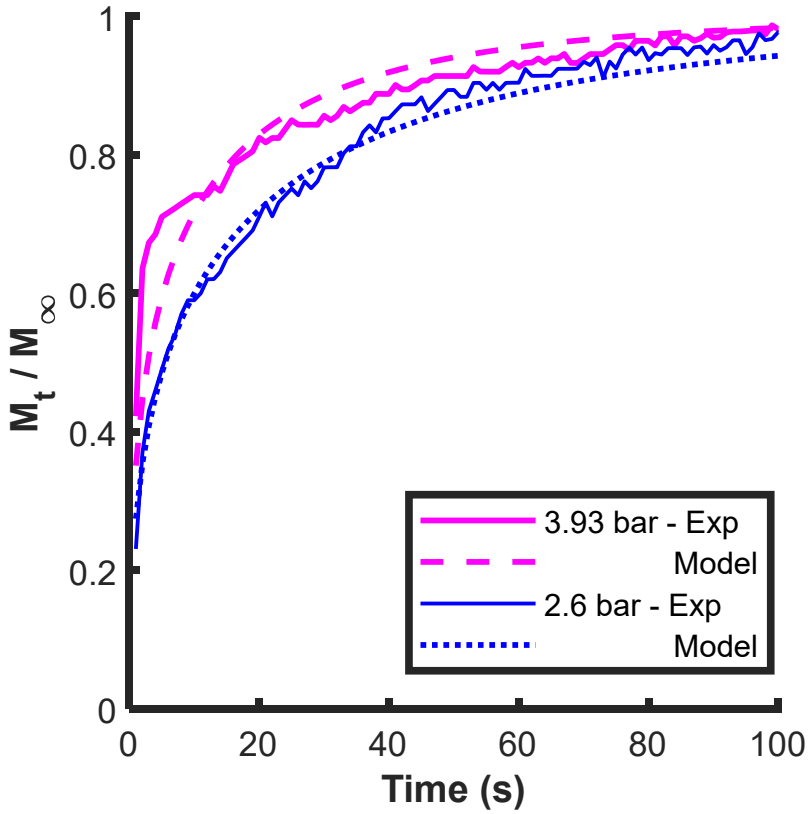


Figure 7. Fitting results of the ternary system $C_2$/ 1C4/ LLDPE at 70°C

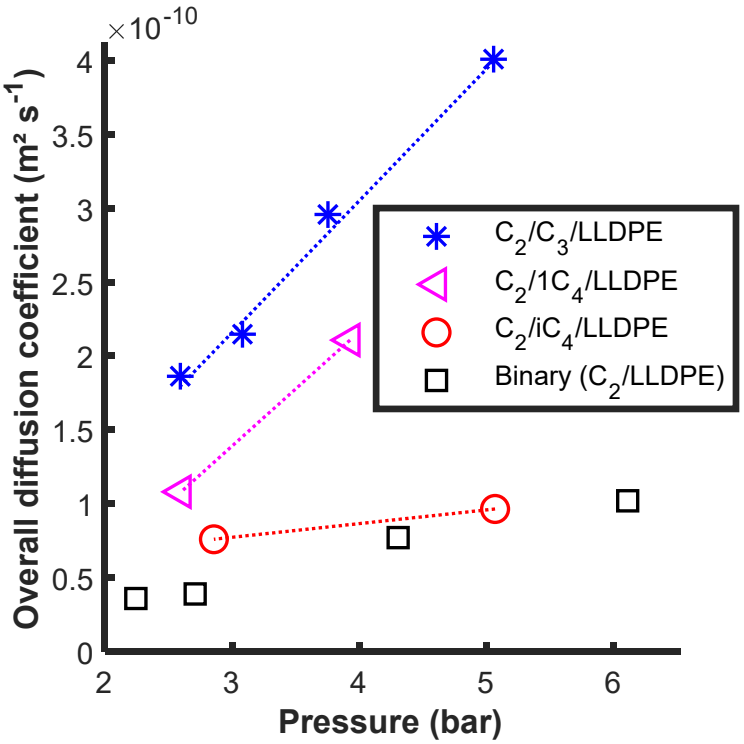


Figure 8. Estimation of the overall diffusion coefficient in different ternary systems in LLDPE at 70°C, compared to binary diffusion of ethylene

As one would expect, the overall diffusivity of all systems increases with increasing total pressure. Furthermore, the overall diffusivity of all ternary systems are higher than the binary system of ethylene/LLDPE, despite the fact that the component added to ethylene is a larger molecule in each case. The pure component diffusivity of alkanes and alkenes decreases as the number of carbons increases, so if the rate of mass uptake was purely additive, one would expect it to decrease upon the addition of propane, iso-butane or 1-butene. This is clearly not what happens. The increase in the diffusivity of the gas mixture can be explained by the same thermodynamic interactions that lead to the cosolubility effect. Adding a co-penetrant increases the free volume of the amorphous phase of the polymer, thereby altering the solubility of the two components and their diffusivities. The co-solubility effect refers to the fact that the heavier component increases the solubility of the lighter one. The lighter component can also decrease the solubility of the heavier one at the same time, but the overall net solubility of the gas mixture is greater than that of the sum of the individual components at the same temperature and partial pressures. Similarly, the co-diffusion leads to an increase of ethylene diffusivity in presence of heavier components, leading therefore to a net increase of the overall diffusivity of the system. However, the magnitude of the effect depends on different conditions, including the solubility of the second species and its molecular size. If we compare the C2+C3 to the C2+1C4 experiments, it can be seen that the impact of propane on the overall diffusivity is much greater than that of 1C4 under similar composition ratios and overall pressures. A little impact of iC4 is observed in these experiments.

Quaternary systems of ethylene as monomer, 1-butene as comonomer and isobutane or propane as ICA in LLDPE-B were also studied. The overall diffusivity of these systems was measured for different pressures up to 6.2 bars at a constant temperature of 70°C. The compositions of the gas phase considered for the quaternary systems are given in Table 3. The sorption curves and data fits are shown in Figure 9 for compositions 1 and 2, and in Figure 10 for compositions 3 and 4. The values of the diffusion coefficients are tabulated in Table 3 and shown in Figure 11.

***Table 3. Quaternary system Ethylene (C2) /Propane (C3) / 1-Butene (1C4) / LLDPE-B (compositions 1 and 2) and quaternary system Ethylene (C2) /isobutane (iC4) / 1-Butene (1C4) / LLDPE-B (compositionss 3 and 4) at 70°C.***

| Molar composition | Total pressure (bar) | D ($m^2$ $s^{-1}$)× $10^{10}$ |
|---|---|---|
| **Composition 1:** | 2.626 | 2.01 |
| $x_{C2}$ = **0.38** | 4.832 | 2.76 |
| $x_{C3}$ = **0.39** | 6.207 | 3.17 |
| $x_{1C4}$ = **0.23** | | |
| **Composition 2:** | 2.613 | 2.62 |
| $x_{C2}$ = **0.41** | 4.14 | 3.15 |
| $x_{C3}$ = **0.42** | 5.557 | 3.54 |
| $x_{1C4}$ = **0.17** | | |
| **Composition 3** | 2.504 | 0.64 |
| $x_{C2}$ = **0.40** | 4.185 | 1.063 |
| $x_{iC4}$ = **0.37** | 5.679 | 1.046 |
| $x_{1C4}$ = **0.23** | | |
| **Composition 4** | 2.864 | 0.61 |
| $x_{C2}$ = **0.40** | 4.604 | 0.87 |
| $x_{iC4}$ = **0.43** | 6.078 | 1.28 |
| $x_{1C4}$ = **0.17** | | |

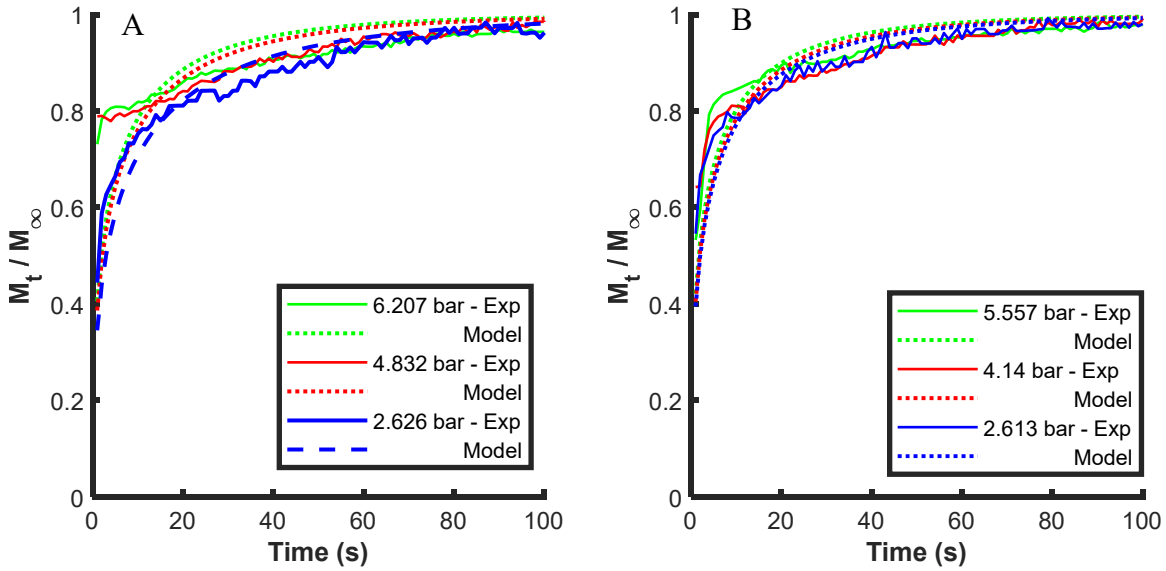


Figure 9. Fitting results of the quaternary system Ethylene (C2) / Propane (C3) /1-Butene (1C4) / LLDPE at 70°C, at two compositions, A: composition 1, B: composition 2.

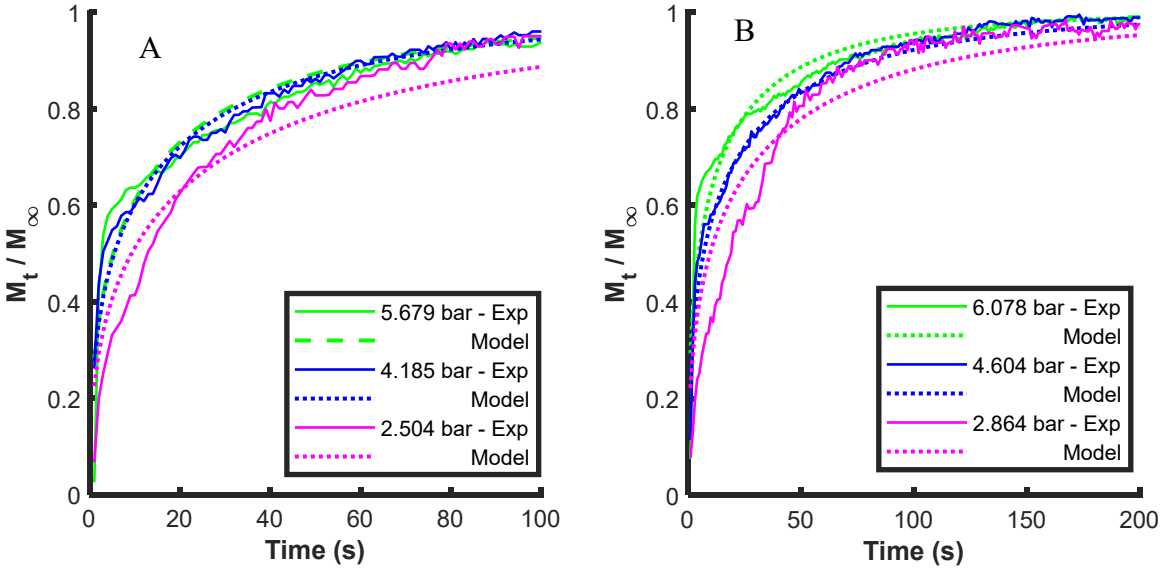


Figure 10. Fitting results of the quaternary system Ethylene (C2) / Isobutane (iC4) /1-Butene (1C4) / LLDPE-B in LLDPE at 70°C, at two compositions: A: composition 3, B: composition 4.

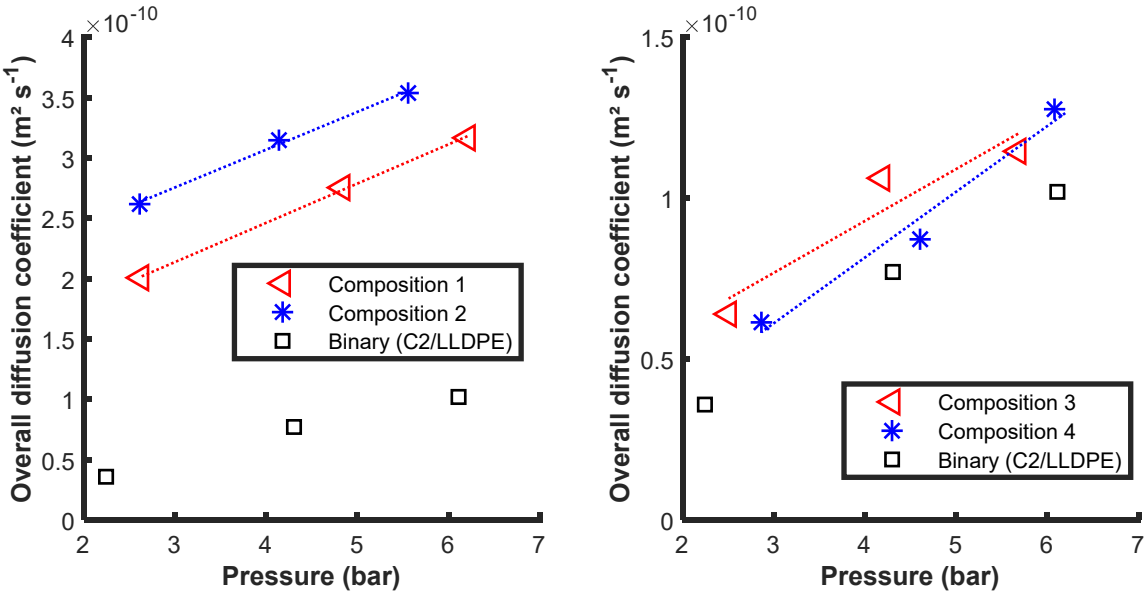


Figure 11. Estimation of the overall diffusion coefficient in the quaternary systems (A) C2/C3/1C4/LLDPE – Compositions 1 and 2 and (B) C2/iC4/1C4/LLDPE – Compositions 3 and 4. Comparison to the binary diffusion coefficient of C2/LLDPE (Table 1). All data at 70°C.

In the system ethylene/propane/1-butene/LLDPE-B at 70°C two different gas phases compositions were considered. The ratio of C2/C3 remains (more or less) constant, but composition 2 has less 1-butene than composition 1. The lower 1-butene fraction corresponds to a higher overall diffusivity, as was observed for the ternary systems above. In the case of

compositions 3 and 4, propane was replaced by the heavier isobutane. Here it can be seen that this leads to a lower overall diffusivity than in the case of propane. It should also be noted that the overall diffusivities measured for compositions 1-3 are higher than the equivalent pure ethylene diffusivity (c.f. Table 1). The diffusivity of composition 4 is very similar to that of ethylene alone at the same overall pressures. Nevertheless, these results suggest once again that the thermodynamic interactions between the components of a mixture of penetrants and the amorphous phase of polyethylene (and most likely polypropylene) are such that a detailed thermodynamic model that allows one to include them is essential for the accurate prediction of the diffusivity.

## 5. Conclusions

A magnetic micro-suspension balance was used to measure the rate of uptake of ethylene and mixtures of ethylene with one or two additional components. The dynamic portion of the sorption, or uptake curves, was used to estimate the overall diffusivity of mixtures of gases in LLDPE, using the assumption that the diffusion characteristic lengths of the particles used in the experiments could be described as a normal distribution of spheres (including variations in the internal structure of each particle as well as differences between the particle sizes). As expected, it is observed that the overall diffusivity of pure ethylene and mixtures of ethylene with other process gases increased as the total pressure of the system increased in all cases. However, it is more important to see that adding another hydrocarbon (here propane, iso-butane and/or 1-butene) leads to an increase in the overall diffusivity of the mixtures despite the fact that the pure diffusivities of the components heavier than ethylene all have lower diffusivities than ethylene. It is interesting to note that iso-butane has a less remarkable effect on the diffusion process than an equivalent amount of 1-butene, in the ternary systems.

This increase was attributed to the co-diffusion effect, analogous to the increase in solubility of ethylene observed in the same experiments (see reference 5). In both cases the addition of a compound heavier than ethylene to a ternary mixture increases the free volume of the amorphous phase of the polymer where transport takes place. Similarly, all but one of the quaternary systems had overall diffusivities notably superior to pure ethylene. It was also observed that the diffusivity of ethylene plus propane was greater than that of ethylene plus iso-butane (or 1-butene) for an equivalent amount of the second compound. Of course, the magnitude of the co-diffusion effect will depend on the composition of the gas phase mixtures, as well as on the nature of the polymer.

This article has thus demonstrated that the composition of the gas phase can have a notable effect on the diffusion process of process gases in polyethylene (and one would suspect that a similar conclusion could be drawn for other polyolefins). It would be useful in the near future to attempt to quantify the experimental observations in this paper with an approach such as the one proposed in reference [7], but a more extensive experimental campaign would be required before we can reliably predict precise values for different gas phase mixtures. Furthermore, as has been pointed out in a recently published study on multicomponent solubility, it will be necessary to account for the macromolecular structure as well, as the degree of crystallinity, as well as the shape of the molecular weight distribution appear to influence the sorption and transport of small molecules in polyethylene.

## 6. Acknowledgement.

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