Determination of diffusion coefficients of alkanes in polyethylene powder by infinite dilution inverse gas chromatography (IGC)

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The diffusion of solvent molecules in polymers can be measured rapidly and accurately by IGC at any concentration. At infinite dilution the van Deemter equation can be applied to obtain bulk diffusion coefficients. This paper demonstrates the performance of IGC measurements for the diffusion of octane in polyethylene.

Introduction

The knowledge of the diffusion rate of solvent molecules through a polymer is important in polymer processing, analysis and performance. Diffusion coefficients are only available for a certain number of polymer solvent systems due to the difficulties in measurement. Usually simple gravimetric measurements are applied on a molten sample of the polymer. These measurements require a relatively large solvent concentration to observe a measurable change in weight. Moreover a single experiment is time consuming.

Inverse gas chromatography (iGC SEA) provides the possibility for a fast and accurate measurement of the solvent vapour diffusion at any required concentration range. Especially in the infinite dilution range iGC SEA is the only reasonable technique to obtain reliable results. This makes iGC SEA a valuable tool in polymer characterisation.

Arnould and Laurence [1] give a good overview about important publications in this field and provide various references.

This paper describes the iGC SEA measurement of solvent diffusion coefficient by means of octane on polyethylene.

Theory

For iGC SEA measurements diffusion effects can be subdivided into gas phase diffusion through a column bed (permeability) and bulk diffusion into a material. iGC SEA provides the possibility to separate these contributions and therefore to measure each. This causes confusion in iGC SEA literature when using the term "diffusion" for both effects. In order to avoid any misunderstanding the gas phase diffusion is called "permeability" in this paper.

For the measurement of the diffusion in a typical iGC SEA experiment a small amount of an organic vapour is injected into a carrier gas stream. At infinite dilution the adsorption is independent of the surface coverage of the adsorbed molecules. The result is a linear adsorption isotherm, which can be described by Henry's Law. In this case the experimentally obtained peaks are symmetrical (Gaussian) and the retention time in the peak maximum can be used to calculate the retention volume. The net retention volumes V_R^0 are computed using Equation 1 where T is the column temperature, m is the mass, F is the exit flow rate at 1 atm and 273.15K, t_R is the retention time for the adsorbing

probe and t0 is the mobile phase hold-up time (dead time). j is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed [2].

The retention volume is measured at different carrier gas flow rates. For a systems that shows bulk sorption the peak width is changing with flow rate due to the dominating diffusion kinetics.

At infinite dilution the van Deemter equation (Equation 2) can be applied.

This equation was originally derived for analytical chromatography and describes the dependence of the theoretical plate height H from the linear flow rate u [3].

A and B are constants representing the eddy diffusion and the molecular diffusion in the gas phase. The constant C describes all effects related to non-equilibrium behaviour. A more detailed description is given in [4].

Figure 1.   Dependence of the theoretical plate height from the linear flow rate (van Deemter

 curve).

Assuming the diffusion in the bulk is the dominating process inside the particle and a uniform packing of particles with a narrow

monomodal particle size distribution with an average diameter d the constant C is directly related to the permeability constant DP (equation 3). k is the partition coefficient.

This equation represents a very general description of the relation but is applicable to various systems [5]. More sophisticated equations are published in literature for particular solvent/polymer systems. The interested reader is again directed to reference [1].

Method

Various columns (SMS standard column with 2mm ID and 30 cm length) were packed with polyethylene powder (PE). The PE as well as the solvent were provided by Aldrich. The mean particle diameter of the PE powder was 10 μm. All sorption experiments were carried out on an SMS-iGC 2000. Measurements were done with octane between 5 and 32 ml/min at 303 K .

Before measurements a pre-treatment was carried out for 10 h at 20 ml/min and the measurement temperature.

Results

Figure 2 shows an experimental curve for the dependence of the retention volume from the flow rate by means of octane sorption on polyethylene. This represents a typical bulk absorption behaviour.
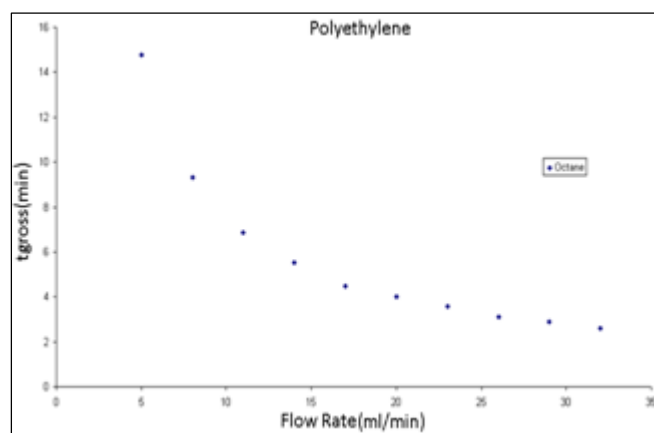

Figure 2. Experimental obtained curve from a measurement with octane at 30oC between 5and 35 ml/min

The C constant can be calculated from a fit of the van Deemter curve using Equation 3. Although a measurement at high flow rates would allow a simplification of Equation 3 the three-parameter fit provides all three constants and therefore to obtain information about gas phase diffusion effects as well. Figure 3 shows the van Deemter plot for octane.
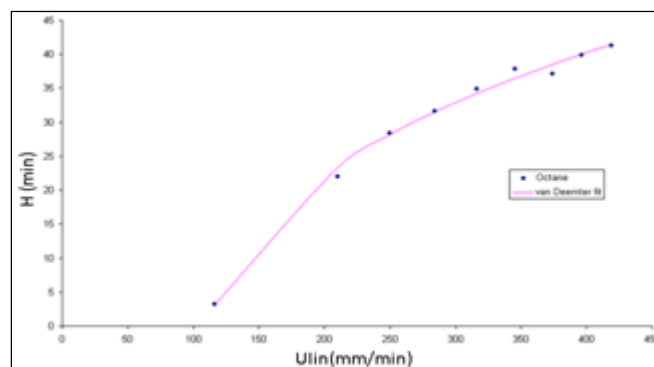

Figure 3. Van Deemter plot for the system octane/polyethylene.

Looking at Figure 3 only the left (raising) part of the van Deemter curve seems to be available even at these low flow rates. This can be explained by the dominating bulk diffusion, which causes a shift of the minimum to the left (smaller flow rates) in the van Deemter curve.

From the C constant the diffusion coefficients can be computed readily using Equation 3.

Table 1 gives the obtained values for octane.

Table 1. Permeability coefficients for octane in polyethylene.

Column	D_P (cm²/sec)
Column 1	$1.5378 \cdot 10^{-8}$
Column 2	$1.3777 \cdot 10^{-8}$

The average value from measurements on two different columns is $1.458 \cdot 10^{-8}$ cm2/sec.

The values obtained for octane are in the same magnitude as typical literature data obtained for a different solvent (decane) on polyethylene ($\sim 0.5 \cdot 10^{-8}$ cm2/sec) [6].

Conclusion

iGC SEA provides an easy and rapid possibility to measure diffusion coefficients of solvents in polymers. Particularly in the infinite dilution range iGC SEA shows clear benefits in comparison to other methods.

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