ELSEVIER

Polymer 43 (2002) 223–226

polymer

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Polymer Communication

The significance of the zero-concentration diffusivity value obtained from integral desorption data

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Received 23 July 2001; received in revised form 20 August 2001; accepted 28 August 2001

Abstract

n-Hexane zero-concentration diffusivity in high density polyethylene obtained 'indirectly' from integral desorption measurements using the free volume concept was compared with the zero-concentration diffusivity obtained directly at low-*n*-hexane activities using a quartz-spring system. The difference between the results obtained by the indirect and direct methods was within the experimental error. The concentration dependence of the diffusivity predicted by the Cohen–Turnbull–Fujita free volume theory was in accordance with experimental data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion; Sorption; Desorption

1. Introduction

Integral sorption and desorption experiments are frequently used to determine diffusion and permeability properties of solutes in polymers [1,2]. The experiment is easy to perform, and this explains its popularity. A typical sorption experiment involved exposing the specimen to a gas/vapour or liquid and at the same time recording its weight increase as a function of time. A typical desorption experiment is performed by exposing the solute-saturated specimen to an environment different from that in which it was saturated and subsequently recording the weight decrease as a function of time. By fitting the weight increase/decrease-time curves to Fick's equation, it is possible to obtain the diffusion coefficient. In cases where the solute solubility is high, the diffusivity generally increases with increasing solute concentration (plasticisation effects) [3]. In these cases, the weight increase/decrease-time data can be fitted to Fick's equation, only if an expression for the solute-concentration-dependent diffusivity is included. The diffusivity is often expressed according to an empirical exponential relationship [3]:

$$D(C) = D_{\mathrm{co}}\,\mathrm{e}^{\alpha c} \tag{1}$$

where D_{co} is the zero-concentration diffusivity and α is the plasticisation power. A particularly powerful exponential expression for describing the solute concentration dependence of D and which also has a theoretical basis is the Cohen–Turnbull–Fujita free-volume equation [4–8]:

$$D_{\mathrm{T}} = A\exp\left(-\frac{B_{\mathrm{d}}}{v_1^{\mathrm{a}}f_1 + v_2^{\mathrm{a}}f_2}\right) \tag{2}$$

where A is a constant, v_1^{a} and v_2^{a} are, respectively, the volume fractions of solute and polymer in the amorphous part of the polymer, f_1 is the fractional free volume of the pure solute and f_2 is the fractional free volume of the amorphous fraction of the pure polymer. B_{d} is a constant that depends only on the size of the penetrant molecule [6] and D_{T} is the thermodynamic diffusivity which is related to the diffusivity extracted from the sorption/desorption curves through a thermodynamic correction:

$$D = \frac{D_{\mathrm{m}}}{1 - v_1^{\mathrm{a}}} = D_{\mathrm{T}}\left(\frac{\partial \ln a_1}{\partial \ln v_1^{\mathrm{a}}}\right) \tag{3}$$

where D_{m} is the mutual diffusivity [5,9] and a_1 is the penetrant activity in the polymer. Using the Flory–Huggins theory, Fels and Huang [10] showed that the activity of the solute absorbed in the non-crystalline part of the polymer is given by:

$$\frac{\partial \ln a_1}{\partial \ln v_1^{\mathrm{a}}} = (1 - v_1^{\mathrm{a}})(1 - 2\chi_{12}v_1^{\mathrm{a}}) \tag{4}$$

where χ_{12} is the Flory–Huggins interaction parameter.

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PII: S0032-3861(01)00595-X

D is obtained by solving Fick's second law for a plate:

$$\frac{\partial v_1}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial v_1}{\partial x}\right) \tag{5}$$

where v_1 is the volume fraction of solute dissolved in the polymer at time t and position x. Eq. (2) is valid only for systems which retain a constant volume on mixing and it implies that D increases with increasing concentration of solute when $f_1 > f_2$. Eq. (2) can be rewritten in order to separate the zero-concentration diffusivity (D_{co}) from the solute-concentration-dependent term (ξ_{c}) [7]:

$$D_{\mathrm{T}} = A\,\mathrm{e}^{-(B_{\mathrm{d}}/f_2)}\,\mathrm{e}\left(\frac{B_{\mathrm{d}}v_1^{\mathrm{a}}(f_1 - f_2)}{f_2(f_2 + v_1^{\mathrm{a}}(f_1 - f_2))}\right) = D_{\mathrm{co}}\xi_{\mathrm{c}} \tag{6}$$

The ability of the solute to plasticise the polymer (cf. Eq. (1)) is quantified by the exponential in the factor ξ_{c}. D_{co} is a very useful parameter since it correlates with the physical structure of the polymer and is sensitive to changes in, e.g. the degree of crystallinity. Changes in morphology as well as in molecular mobility due to cold drawing or chemical crosslinking are readily detectable by changes in D_{co} [11]. The zero-concentration diffusivity has also become useful as a tool for validating solute diffusion data modelled by molecular dynamics techniques [12,13]. The question now is, how well does D_{co} obtained from integral desorption measurements, which normally cover the complete solute activity range (0–1) within a single experiment, agree with the directly measured D_{co}, i.e. the diffusivity when the solute concentration approaches zero? The question is important because integral sorption/desorption measurements are commonly used to obtain transport property data, including D_{co} [2]. In order to answer this question, *n*-hexane integral desorption data from liquid-*n*-hexane-saturated polyethylene specimens are here compared with sorption/desorption data for the same system at *n*-hexane activities close to zero.

2. Experimental

2.1. Materials

The polyethylene grade was an extrusion-coating grade (HE7541, kindly supplied by Borealis AB, Sweden) with a density of 941 kg m^{-3}, a melting peak temperature of 130°C and a melt flow index of 7.5 g/10 min (ISO 1133). The polymer was compression moulded into 65 ± 5 and 23 ± 2 μm thick films using a Schwabenthan Polystat 400s compression-moulding machine. In this way, both types of films were exposed to the same thermal treatment. The volume crystallinity was 59.3%. *n*-Hexane (purity 99%; density $\rho_1 = 656$ kg m^{-3} at 25°C) was obtained from Merck.

2.2. Integral desorption

The film was first immersed in liquid *n*-hexane at 25 and 37°C until sorption equilibrium was attained. The saturated film was then exposed to air at 25 and 37°C and the desorption kinetics were monitored by intermittent weighing of the specimen on a Mettler AE balance. The numerical procedure for fitting the integral desorption curve is described in Refs. [3,8,14].

2.3. Low activities differential sorption/desorption experiments

Vapour sorption/desorption experiments in polymeric films at low penetrant activities were performed, using a quartz spring balance to measure the sample mass during the experiments. Polyethylene films about 10 mg in weight and 23 μm thick were used in the experiments. The spring with the sample was placed in a glass jacketed column where the gas pressure can be set up to 1 atm and measured with a precision of 10^{-2} mbar. Water in the jacket of the column was used to keep the temperature of the system within 0.2°C with respect to the target value of 37°C. The spring elongation was measured by means of a DVT CCD camera, which monitored the sample position in the column. Analysis of the image obtained from the camera enabled variations in the mass of the sample as low as 1 μg to be evaluated. Sorption experiments were conducted by first degassing the column. Thereafter a small amount of vapour was entered into the column and the vapour pressure was recorded. The mass increase (spring extension) was monitored as a function of time and from this curve the diffusion coefficient and solubility, corresponding to the actual concentration (vapour pressure) range was evaluated. After sorption equilibrium was attained, more vapour was allowed to enter into the column and the procedure for evaluating the diffusivity and solubility was repeated. Desorption experiments were conducted by emptying the chamber in steps and at each step monitoring the spring getting shorter as a function of time.

3. Results and discussion

Fig. 1 shows the solubility of *n*-hexane at 37°C as a function of the *n*-hexane activity. From the data, $\ln(a_1)$ was plotted as a function of $\ln(v_{1\mathrm{a}})$ (insert in Fig. 1) and the curve was subsequently fitted to a second-order polynomial. From the polynomial the derivative: $(\partial \ln a_1)/(\partial \ln v_1^{\mathrm{a}})$, was obtained:

$$\frac{\partial \ln a_1}{\partial \ln v_1^{\mathrm{a}}} = \left\{\begin{array}{ll} -0.1142\ln(v_1^{\mathrm{a}}) + 0.5077 & \text{if } v_1^{\mathrm{a}} \geq 0.007 \\ 1 & \text{if } v_1^{\mathrm{a}} < 0.007 \end{array}\right\} \tag{7}$$

If the above derivative is set to 1 at low activities (see the slope in the insert of Fig. 1), the thermodynamic correction vanishes at $v_1^{\mathrm{a}} \rightarrow 0$. Eq. (7) was used in Eq. (3) when fitting the integral desorption data. Fig. 2 presents integral desorption data at 37°C and also, for comparison, at 25°C.

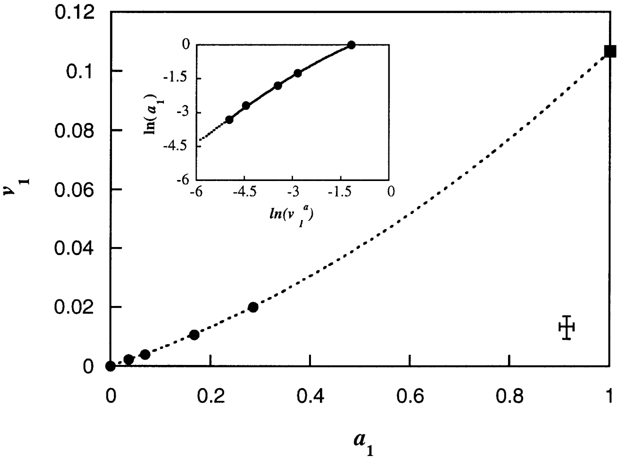

Fig. 1. Saturation volume fraction of *n*-hexane as a function of *n*-hexane activity (●). The data (■) refer to the specimen exposed to liquid *n*-hexane. The insert shows the trend in $\ln(a_1)$ as a function of $\ln(v_1^a)$ (●), fitted with a second order polynomial (line). The dotted line in the insert represents the slope = 1.

The thermodynamic correction at 25°C was considered by using Eq. (4) with an interaction parameter estimated from Eq. (8), an expression proposed by Rogers et al. [15]:

$$\chi_{12} = 1.22(1 - v_1^a)^{-5/3} - 0.61 \tag{8}$$

The fitting of the data obtained at 25°C yielded $D_{co} = 1.4 \times 10^{-9}$ cm^2/s and a polymer fractional free volume equal to 0.0446. $f_1 = 0.168$ was taken from Fleischer [6]. The fractional free volume of *n*-hexane (f_1) at 37°C was estimated from the value at 25°C and the temperature dependence of f_1 [16]. The fit of the data at 37°C yielded $D_{co} = 7.2 \times 10^{-9}$ cm^2/s and $f_2 = 0.057$. The difference: $\Delta f = f_1 - f_2$, increased with increasing temperature but the plasticisation power, which is proportional to $\Delta f / f_2^2$, decreased with increasing temperature. This is observed in Fig. 2 as a sharper and less smooth curvature of the 37°C-curve compared to that of the 25°C-curve. Thus, the free volume theory most beautifully predicts the experimentally observed temperature-dependence of the plasticisation power. Although the difference between f_1 and f_2 generally increases with increasing temperature, the plasticisation power decreases with temperature [9,17–19].

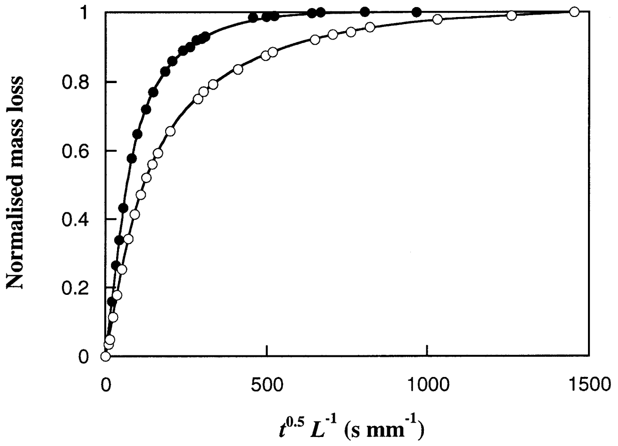

Fig. 2. Normalised *n*-hexane mass decrease as a function of time at 37°C (●) and 25°C (○). Lines correspond to best fits of Eqs. (5) and (6).

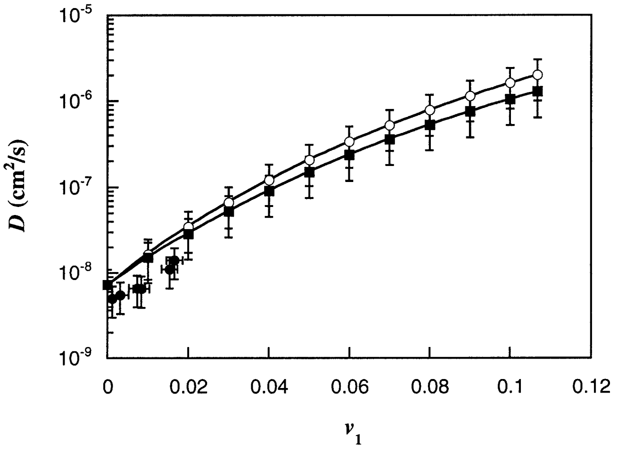

Fig. 3. *n*-hexane diffusivity as a function of the volume fraction of *n*-hexane measured at low *n*-hexane activity ($\bar{D}$, ●) and determined indirectly from integral desorption measurements using the free volume theory with: D_T (●) and without: $D_T(\partial \ln a_1 / \partial \ln v_1^a)$ (○) thermodynamic correction.

In the analysis of the kinetics of each differential sorption or desorption run, the assumption was made that the diffusion coefficient can be considered to be constant; this assumption is indeed acceptable in view of the low change in solute concentration which takes place during a differential run. Through this analysis, the average diffusion coefficient $\bar{D}$ in each differential run was obtained, and related to the average solute concentration (v_1^a) in the run in such a way as to obtain the function $\bar{D}(v_1^a)$. In order to validate the zero-concentration diffusivity D_{co} from the integral desorption experiments, it was compared with the average diffusivity at the lowest concentration obtained from differential sorption/desorption experiments.

Fig. 3 shows the diffusivity obtained 'indirectly' from integral desorption data and the diffusivity obtained 'directly' at low *n*-hexane activity. The diffusivity obtained directly is somewhat lower than the integral desorption diffusivity over the whole concentration range. From the low-activity measurements $D_{co}(\bar{D})$ was estimated to be 5×10^{-9} cm^2/s, which was 30% off from the integral value obtained above ($D_{co} = 7.2 \times 10^{-9}$ cm^2/s). The amount of material dissolved by hexane in the integral experiments was very small, <0.5%. Still the fact that the sample in the integral desorption analysis was exposed to a liquid rather than a vapour could be part of the reason that integral desorption measurements yielded higher values. The difference was however within the experimental error (Fig. 3).

Interestingly, the concentration dependence of the diffusivity (slope in Fig. 3), as described by the free volume theory (Eq. (6)), was similar to that given by the experimental data (direct method). Thus the free volume theory, applied to integral desorption data, provides an accurate estimate of both the concentration dependence of the diffusivity and the rate at which solute molecules move in the dry polymer (zero-concentration diffusivity).

Acknowledgements

Dr Marco Giacinti at the Department of Chemical Engineering, Mining and Environmental Technologies, University of Bologna, is thanked for experimental assistance with the quartz-balance system.

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