Diffusivity of Alcohols in Amorphous Polystyrene

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ABSTRACT: Gravimetry is used to study the diffusion of a homologous series of alcohols (C_n, with $n = 1, 2, 3, 4, 6, 10,$ and 16) in amorphous polystyrene at temperatures from 35 to 145°C, that is both below and above the polymer glass transition temperature of 100°C. All the mass uptake results are well described by a simple Fickian model (for $t < t_{1/2}$) and are used to calculate the corresponding diffusion coefficients using the thin-film approximation. At any particular temperature, the alcohols C_n with $n = 3, 4,$ and 6 possess very similar diffusivities despite the fact that the chain length doubles from C_3 to C_6. This peculiar diffusivity behavior is explained based on the variation of the polymer–solvent chemical affinity along the homologous series. As expected, at any particular temperature, the diffusivity decreases considerably from C_6 to C_{10} and from C_{10} to C_{16}. For each alcohol, its $\log(D)$ increases linearly with the decrease in liquid viscosity associated with an increase in temperature. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Understanding the diffusion of small molecules in polymeric materials is important to advanced polymer technologies such as membrane separations,[1–3] barrier materials,[1–3] controlled drug release,[2] biosensors,[2] and chemical sensors.[4–6] For these reasons, the diffusion of gases and liquids through polymer membranes has been the subject of intense research over the last decades.[1–3,7] Several different experimental techniques have been previously used to measure diffusion coefficients. These include Fourier transform infrared spectroscopy (FTIR),[8–11] Nuclear magnetic resonance (NMR),[12–15] neutron and X-ray reflectivity measurements,[16] electrical impedance spectroscopy,[17] secondary ion mass spectrometry,[18] fluorescence spectroscopy,[19] light microscopy,[20] and mass uptake measurements.[21–23]

Mass uptake measurements have proved to be a reliable technique to measure diffusion coefficients.[21–23] In general, the mass uptake in polymer–penetrant systems has been demonstrated to follow a power law expression of time of the form:

$$\frac{M_t}{M_\infty} = Kt^n \tag{1}$$

where M_t and M_∞ are the experimental mass uptakes at times t and ∞, respectively; K is a constant and n is an exponent related to the transport mechanisms as follows: $n = 0.5 \Rightarrow$ Fickian transport; $n = 1.0 \Rightarrow$ Case II transport, and $0.5 < n < 1.0 \Rightarrow$ anomalous diffusion. In these three categories of diffusion behavior, the rate of diffusion of solvent is much less than, much greater than, or comparable to the rate of polymer segmental relaxation, respectively.

Several attempts have been made so far to correlate the diffusion properties with characteristic parameters of the diffusing molecules. Free-volume theories have been developed[24–31] but they usually require a large number of input modeling parameters which are usually only available for a very limited number of systems. Molecular simulations have also been used to correlate diffusion properties with molecular parameters.[32–34] An alternative approach to the diffusion analysis, one which will be used in the present study, has been based on semi-empirical correlations between the diffusion coefficient and the physicochemical properties of the diffusing molecules. Some parameters which are known to play an important influence on the rates of liquid diffusion inside polymer matrices are the temperature, the liquid viscosity, the shape and size of the penetrant molecules, as well as the chemical affinity between the polymer matrix and the penetrant molecule.

The temperature dependency of diffusion coefficients has been extensively investigated in the past and has been most commonly described by an Arrhenius equation:

$$D = D_0 \, \exp \, (-E_D/RT) \tag{2}$$

In this equation, E_D is the activation energy of diffusion. This equation has proved to be of quite general applicability for gases and small-molecule liquid penetrants over relatively small temperature intervals $(25-70°C)$[32,35–38] although some deviations have also been reported including a change of slope at the polymer glass transition temperature.[21,39]

The diffusion coefficients D for various liquids diffusing in natural rubber at 25°C have been shown to depend on their corresponding liquid viscosities η,[40,41] through a relationship of the type $log \, D \, \alpha \, log \, \eta$, and a new diffusion mechanism has been recently proposed which takes explicitly into account the viscosity of the liquid penetrant.[42]

The shape of the penetrant molecule has also been shown[21,38] to play an important role in determining its rate of transport within the polymer matrix. For instance, flattened or elongated penetrant molecules have much higher diffusion coefficients, by a factor of up to 10^3, than spherical molecules of equal molecular volume, implying that elongated penetrant molecules (anisometric molecules) move primarily along their long dimension during diffusion through a polymer.[38] Although there is, for small gas (spherical) molecules, an inverse proportionality between log D and the penetrant mean diameter, for elongated penetrant molecules the correlation is more complex[38] and no general expression exists which can correlate satisfactorily the diffusion coefficient with the shape of the penetrant molecule.

The dependence of the diffusion coefficients of identically shaped molecules on their size (number of C atoms, molecular weight, molecular volume) has also been a topic of research.[21,35,43] In the case of the diffusion of long polymer chains in the melted state, this problem has been solved by de Gennes who introduced the concept of reptation which states that the overall friction coefficient of a linear polymer chain in the melt is proportional to its length. Reptation gives a diffusion coefficient that decreases as the square of the length of the diffusing molecule, $D \propto n^{-2}$. In the case of the diffusion of shorter chains in glassy polymers, still no general expression exists which can correlate satisfactorily the diffusion coefficient with the size of the penetrant molecule, despite the fact that several different correlations have been proposed. Chen and Ferry[37] studied the diffusion of n-dodecane and n-hexadecane through rubbery polymers and concluded that the diffusion coefficients (D) for the two penetrants were approximately inversely proportional to their molecular lengths. Mills and Kramer[44] on studying the diffusion at 25°C of a series of 1-iodo-n-alkanes liquids into a polymer glass photoresist found that for the larger values of number of carbon atoms (n), the solvent's diffusion coefficient (D) decreases as n^{-2} prompting speculation that the longer chains ($n \geq 4$) diffuse into the glass by a reputation-like mechanism. Gall et al.[45] also studied the diffusion of a series of 1-iodo-n-alkanes vapors in polystyrene and they found that the solvent's diffusion coefficient D decreased exponentially with increasing the number of carbon atoms on the alkyl chain. Contrary to Mills and Kramer[44], Gall et al.[45] have found no evidence for a reptation-like mechanism.

Storey et al.[21] on studying the diffusion of dialkyl phthalate plasticizers in PVC concluded that ln(D) decreases approximately linearly with respect to the number of carbon atoms in the n-alkyl chain. Ward and coworkers[46,47] studied the effect of penetrant size, shape, and chemical nature on the diffusion of n-alkanes (ranging from C_6 to C_{17})[46] and esters[47] through a thermoset adhesive and they concluded that the mechanism of n-alkanes and esters diffusion is Fickian. They used a power law expression of the form $D = bM^a$ (log D = log b + a log M) to describe the dependence of the diffusion coefficient D on the molecular size M of the penetrant molecule, with a and b being material parameters. This power law was able to describe successfully, as a function of molecular size M, the diffusion coefficients of alkanes[46] but it failed to describe the diffusion coefficients of esters,[47] according to the authors, owing to the specific chemical interactions involving the esters.

Despite all these efforts just described, no simple and general correlation is currently available to describe the diffusion of solvents through polymeric materials, which justifies a continuing effort in this fundamental research field. In a previous publication,[48] the equilibrium sorption of alcohols in polystyrene has been studied, over a large range of temperatures. The present study reports a systematic study of the sorption kinetics of the homologous series of linear 1-alcohols (namely methanol (C_1), ethanol (C_2), 1-propanol (C_3), 1-butanol (C_4), 1-hexanol (C_6), 1-decanol (C_{10}), and 1-hexadecanol (C_{16})) in an amorphous polystyrene film, over a broad range of temperatures.

EXPERIMENTAL

Materials and Equipment
The polystyrene utilized in the present study was bought from Sigma-Aldrich, Madrid, Spain (catalogue no. 43,010-2). It is identical to the polystyrene used in the previous studies,[48–51] it has an average M_w ca. 230,000 and average M_n ca. 140,000 and its FTIR and ^{1}H-NMR spectra have been previously reported.[49] All the alcohols used in this study were bought from Alfa-Aesar, Karlsruhe, Germany and had purities of $\geq 99\%$.

Gravimetric Method
Rectangular-shaped flat samples of polystyrene with average dimensions $16.0 \times 14.0 \times 0.8$ cm were compression molded, using mold cavities with the appropriate dimensions. The length, width, and thickness of all the samples were measured using a micrometer with precision ± 0.001 cm and the weight of all the samples was measured using an analytical balance with precision ± 0.0001 g.

The samples were placed in a convection oven (Brand name: MMM; Model: Venticell 55) containing diffusion bottles with preheated solvent. The temperature inside the oven was highly constant and homogeneous and measured with a precision of $\pm 1°C$. The samples were removed from the diffusion bottles at short diffusion times ($t < t_{1/2}$, being $t_{1/2}$ the time at half saturation) and their surfaces were gently cleaned with absorbent paper to remove any solvent from the surface and then they were weighted immediately to the nearest ± 0.1 mg. In those systems in which the penetrant was liquid at room temperature (i.e., all except 1-hexadecanol) the samples after being removed from

the oven, and before being cleaned with absorbent paper, were quenched to room temperature by adding large excess amount of the corresponding liquids at room temperature ($\sim 23°C$). In the case of methanol, 1-propanol and 1-butanol weighting bottles were used to reduce the experimental error owing to possible evaporation during weighting. In the case of 1-hexanol and 1-decanol, the use of a weighing bottle was not necessary because these two alcohols have extremely low vapor pressures at room temperature. In the case of 1-hexadecanol, it is a solid at room temperature and therefore the samples after being removed from the oven were simply allowed to cool down naturally to room temperature and then the excess 1-hexadecanol solidified on the PS surface was very easily removed, for example by scratching with a spatula.

For each polymer–solvent system at each temperature, at least five different samples have been tested.

RESULTS AND DISCUSSION

All of the samples had an aspect ratio (length over thickness) of >10, which ensured application of one-dimensional diffusion equations for the analysis of the transport data.[52]

The first step in the analysis of the sorption data was to verify if the sorption process conforms to a known transport mechanism. The Fickian nature of the sorption data was confirmed from the reduced sorption plots for these systems, that is plots of either $M_{ALKANE}(t)/M_{PS}$ or $M_{ALKANE}(t)/M_{ALKANE}(\infty)$ *versus* the square root of time normalized by the film thickness, 2L. Examples of such plots for the diffusion of several alcohols at different temperatures, both below and above the polymer T_g (100°C), are shown in Figure 1. All the curves in Figure 1 show an initial linear increase with time $t^{1/2}$ followed by a smooth approach to equilibrium represented by the plateau regions. The curves obtained at different test temperatures, irrespective of being either below or above the polymer T_g, were found to be all similar in shape and to possess the Fickian characteristic of linearity at least up to 50% fractional mass uptake ($M_t/M_\infty = 0.50$).

Equation (3) represents the mass uptake governed by Fick's Law for double-sided sorption in a flat film of thickness 2L, where it is assumed that the film is so thin (2L $\ll$ length and width) that effectively all the diffusing substance enters through the plane faces and a negligible amount through the edges[52]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 \pi^2 Dt}{4l^2}\right] \quad (3)$$

M_t is the mass uptake at time t, M_∞ is the amount absorbed at equilibrium, and D is the diffusion coefficient.

After confirming the Fickian nature of the diffusion process and using the experimental results obtained, the "Mass Uptake per Area per sqrt(time)," hereafter simply referred by the letter Z, have been determined for each system at each temperature using the relationship:

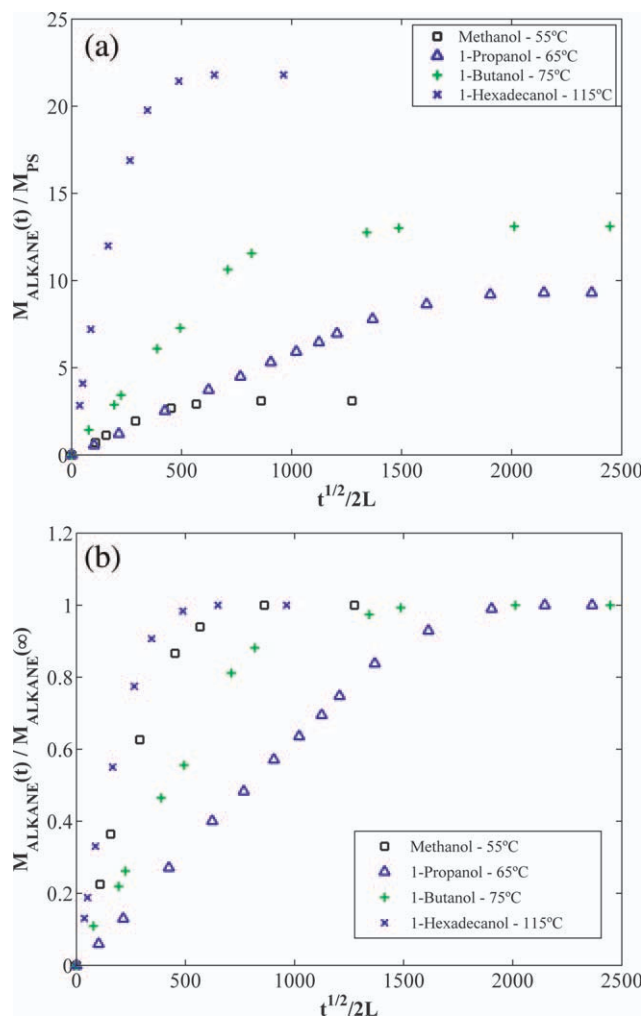$$Z = \frac{\text{Mass uptake}(t)}{2 * \text{Area} * \text{sqrt}(t)} \quad (4)$$

Figure 1. Sorption plots for linear alcohols at several different temperatures (both below and above the T_g of polystyrene): ($\square$) methanol at 55°C, (Δ) 1-propanol at 65°C, (+) 1-butanol at 75°C, and (X) 1-hexadecanol at 115°C. The curves obtained for all the other systems not represented here are similar to these ones, that is they possess the Fickian characteristic of linearity at least up to 50% fractional mass uptake. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where time $t < t_{1/2}$. In eq. (4) "area" is the area of each face and the factor 2 accounts for the fact that each flat sample has two identical faces. As mentioned before, considering the high aspect ratio of the samples, any residual diffusion through the sample edges can be safely ignored. In eq. (4), Z has the units g cm^{-2} s$^{-1/2}$. If it is assumed, as is usually considered to be a valid assumption, that polymer and liquid volumes are additive, then the rates of mass uptake as expressed in eq. (4) can be considered as directly related to the rates of polymer swelling. Therefore, for a particular polymer–solvent system, the higher the value of Z is, the higher is the rate of polymer swelling in that solvent at the specified temperature.

The results obtained for Z are summarized in Table I and they are plotted in Figure 2 as log(Z) as a function of temperature. The values of Z are directly proportional to the slopes of the mass uptake curves shown in Figure 1(a). As summarized in

Table I. Mass Uptake Per Area Per Sqrt(Time)

Temperature (°C)	Mass uptake per area per sqrt(time) (mg cm^{-2} s$^{-1/2}$)						
	C_1	C_2	C_3	C_4	C_6	C_{10}	C_{16}
35	0.0021	–	–	–	–	–	–
45	0.0033	–	–	–	–	–	–
55	0.0043	0.0017	0.0013	0.0010	–	–	–
65	0.0069	0.0033	0.0036	0.0038	0.0035	0.0020	–
75	–	0.0070	0.010	0.012	0.012	0.0052	–
85	–	–	0.029	0.034	0.034	0.015	0.0045
95	–	–	0.058	0.075	0.075	0.035	0.011
105	–	–	–	0.13	0.14	0.075	0.025
115	–	–	–	0.22	0.24	0.14	0.055
125	–	–	–	–	–	0.23	0.095
135	–	–	–	–	–	–	0.16
145	–	–	–	–	–	–	0.25

Each value in this table is the average of at least five different measurements. These values are shown in Figure 2.

Table I, the values of Z (in μg cm^{-2} s$^{-1/2}$) for the systems represented in Figure 1(a) are Z(methanol, 55°C) = 4.3, Z(1-propanol, 65°C) = 3.6, Z(1-butanol, 75°C) = 12, and Z(1-hexadecanol, 115°C) = 55. These values are in agreement with the different slopes (for $t < t_{1/2}$) observed for the different curves in Figure 1(a). As clearly shown in Table I and Figure 2, and as expected, the rates of mass uptake increase with temperature for all the systems. Also, in general, for each temperature, the rates of mass uptake usually decrease when the chain length increases from one carbon atom (methanol) to 16 carbon atoms (1-hexadecanol). However, some exceptions on this occur between ethanol, 1-propanol, 1-butanol, and 1-hexanol. These exceptions which constitute apparent abnormalities are owing to the fact that the equilibrium sorption values increase from methanol to 1-hexanol as reported previously[48] and as will be discussed in further detail, below.

For short diffusion times, $(M_t/M_\infty) < 0.5$, eq. (3) may be approximated by:

$$\frac{M_t}{M_\infty} = \frac{4}{l}\left[\frac{Dt}{\pi}\right]^{\frac{1}{2}} \quad (5)$$

From a plot of M_t versus $t^{1/2}$, a single master curve is obtained which is initially linear. Thus, D can be calculated from a rearrangement of eq. (5) as:

$$D = \pi\left[\frac{h\theta}{4M_\infty}\right]^2 \quad (6)$$

In eq. (6), θ is the slope of the initial linear part of the graph of M_t versus $t^{1/2}$; h is the sample thickness and M_∞ is the equilibrium solubility, whose values have been reported previously.[48] This approach to the calculation of diffusion coefficients has been extensively used earlier.[35,46,47] Alternatively, the diffusion coefficients can be determined from the previously determined Z-values, using the relationship:

$$D = \frac{2500\,\pi}{d^2}\left(\frac{Z}{S}\right)^2 \quad (7)$$

where d is the polystyrene density at the specified temperature (g cm^{-3}), Z is the Mass Uptake per Area per sqrt(time) (g cm^{-2} s$^{-1/2}$) and S is the solubility value $M_L(\infty)/M_{PS}$, expressed in percentage weight, at the specified temperature. The values of S, as obtained in the previous study,[48] are listed in Table II.

According to the literature,[53] the density of polystyrene varies with temperature according with the relationships:
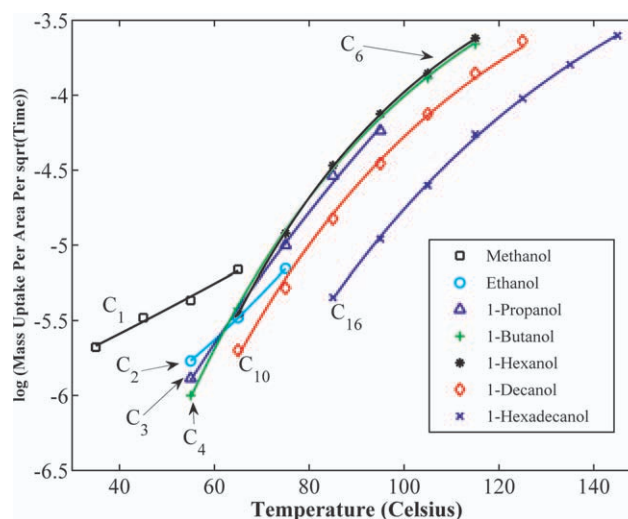

Figure 2. Mass Uptake per Area per sqrt(Time) (g cm^{-2} s$^{-1/2}$) for alcohols in polystyrene at several different temperatures: (□) methanol (C1), (O) ethanol (C2), (Δ) 1-propanol (C3), (+) 1-butanol (C4), (*) 1-hexanol (C6), (◇) 1-decanol (C10), and (X) 1-hexadecanol (C16). Assuming that polymer and liquid volumes are additive, this figure represents also the rates of polymer swelling in different liquids at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Equilibrium Saturation Values[a] for Alcohols in Polystyrene at Different Temperatures

Temperature (°C)	Equilibrium saturation (solubility) values—$100(M_L(\infty)/M_{PS})$						
	C_1	C_2	C_3	C_4	C_6	C_{10}	C_{16}
35	–	–	–	–	–	–	–
45	–	–	–	–	–	–	–
55	3.1	4.6	–	–	–	–	–
65	3.4	5.7	9.3	11.4	–	–	–
75	–	7.6	11.0	13.1	14.9	11.7	–
85	–	–	13.3 (*)	15.9 (*)	18.1	14.5	–
95	–	–	16.4	20.5	23.3	18.9	12.4
105	–	–	–	25.3	30.2	23.6 (*)	16.3 (*)
115	–	–	–	35.0	42.7	32.6	21.8
125	–	–	–	–	56.3	42.9	28.9
135	–	–	–	–	–	56.3	39.4 (*)
145	–	–	–	–	–	83.5	53.8

[a]Values with (*) have been obtained by exponential interpolation. These values are required for the calculation of the diffusion coefficients from mass uptake values. Reproduced with permission from Bernardo and Vesely, Eur Polym J, 2007, 43, 938.

$$\frac{d\rho}{dT}(\text{g.cm}^{-3}.\text{K}^{-1}) = -2.65 \times 10^{-4} \quad < T_g$$
$$\frac{d\rho}{dT}(\text{g.cm}^{-3}.\text{K}^{-1}) = -6.05 \times 10^{-4} \quad > T_g \tag{8}$$

The density of the polystyrene samples, as measured using a density bottle at 20°C, is 1.045 g cm^{-3} (average of the measurement of five different samples), which is in agreement with the value 1.05 g cm^{-3} reported in the literature.[54] Furthermore, the T_g of the polystyrene used, as determined by differential scanning calorimetry, is 100°C which is also in good agreement with literature values.[53] Therefore, in the following discussion it will be assumed that the density of the polystyrene samples varies with temperature according to the relationships:

$$d(\text{g.cm}^{-3}) = 1.045 - 2.65 \times 10^{-4}(T - 20) \quad T \leq 100°\text{C}$$
$$d(\text{g.cm}^{-3}) = 1.0238 - 6.05 \times 10^{-4}(T - 100) \quad T \geq 100°\text{C} \tag{9}$$

Along this study, these relationships are used to determine the thermal expansion of the PS samples as a function of temperature. It is assumed that thermal expansion occurs only normal to the samples surfaces, that is any increase in surface area is completely negligible and only an increase in thickness is considered.

The values of D determined using either eq. (6) or (7) (both produce the same results) are listed in Table III. Values of D determined taking into account the thermal expansion of polystyrene are shown outside brackets together with the respective values ignoring the thermal expansion (inside brackets). As

Table III. Diffusion Coefficients (D) of Alcohols in Polystyrene[a]

Temperature (°C)	Diffusion coefficients $\times 1 \times 10^8$ (cm^2 s^{-1})						
	C_1	C_2	C_3	C_4	C_6	C_{10}	C_{16}
55	1.4 (1.4)	0.10 (0.098)	–	–	–	–	–
65	3.0 (3.0)	0.25 (0.24)	0.11 (0.11)	0.082 (0.080)	–	–	–
75	–	0.63 (0.61)	0.61 (0.59)	0.62 (0.60)	0.48 (0.47)	0.15 (0.14)	–
85	–	–	3.5 (3.4)	3.4 (3.3)	2.6 (2.5)	0.80 (0.77)	–
95	–	–	9.3 (9.0)	10 (9.6)	7.7 (7.5)	2.6 (2.5)	0.59 (0.57)
105	–	–	–	20 (19)	16 (15)	7.6 (7.3)	1.8 (1.7)
115	–	–	–	30 (28)	24 (23)	14 (13)	4.9 (4.6)
125	–	–	–	–	–	22 (21)	8.3 (7.8)
135	–	–	–	–	–	–	13 (12)
145	–	–	–	–	–	–	17 (16)

[a]Inside brackets: values not corrected for the thermal expansion of polystyrene. D-values have been determined only for those systems where saturation values (either determined experimentally or interpolated) are known. These values are shown graphically in Figure 3.
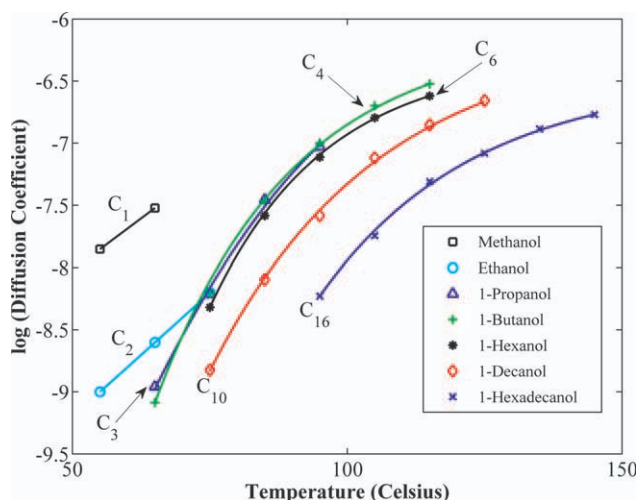
Figure 3. Diffusion coefficients (cm^2 s^{-1}) for alcohols in polystyrene at several different temperatures: (□) methanol (C1), (O) ethanol (C2), (Δ) 1-propanol (C3), (+) 1-butanol (C4), (*) 1-hexanol (C6), (◇) 1-decanol (C10), and (X) 1-hexadecanol (C16). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown, consideration of the effect of thermal expansion produces a very small difference on the final D values obtained. The values of D are proportional to the slopes of the mass uptake curves shown in Figure 1(b). As listed in Table III, the values of $D \times 10^8$ (in cm^2 s^{-1}) for the systems shown in Figure 1(b) are as follows: D(methanol, 55°C) = 1.4, D(1-propanol, 65°C) = 0.11, D(1-butanol, 75°C) = 0.62, and D(1-hexadecanol, 115°C) = 4.9. These values are in agreement with the different slopes (for $t < t_{1/2}$) observed for the different curves in Figure 1(b). The values of D corrected for the thermal expansion of polystyrene are also plotted in Figure 3 as a function of temperature.

As shown in Figure 3, the diffusion coefficients of methanol and ethanol are less temperature dependent than the diffusion coefficients of all the remaining alcohols. This can be easily explained if it is assumed that the minimum void volume needed for the movement of methanol and ethanol molecules is less than the average void volume of the system. In that case, the diffusion of these penetrants occurs by movement of the solvent molecules into pre-existing cavities being therefore less temperature dependent. Larger molecules cannot easily enter into pre-existing cavities and therefore their diffusion coefficients are more temperature dependent because the average void volume of the system increases with temperature. The alcohols C$_3$, C$_4$, and C$_6$ have very similar diffusivities despite the fact that from C$_3$ to C$_6$ the chain length doubles. This peculiar diffusion behavior is certainly related with the sorption behavior reported previously[48] and summarized in Table II. At any particular temperature, the solubility of alcohols in polystyrene increases from C$_1$ to C$_6$, that is S(C$_1$) < S(C$_2$) < S(C$_3$) < S(C$_4$) < S(C$_6$), and then decreases from C$_6$ to C$_16$, that is S(C$_6$) > S(C$_10$) > S(C$_16$). Therefore, the peculiar diffusion behavior observed is easily explained by the fact that from C$_3$ to C$_6$ the increase in polymer–liquid chemical affinity (which favors diffusion) is enough or nearly enough to compensate the corresponding increase in stereochemical hindrance (which unfavors diffusion) involved in the diffusion of the longer solvent chains. Basically, from C$_3$ to C$_6$ the effects of polymer–solvent chemical affinity and seterochemical hindrance are opposing and nearly canceling each other. As also shown in Figure 3, at any particular temperature, from C$_6$ to C$_10$ and from C$_10$ to C$_16$ the diffusivities decrease considerably despite the fact that, comparatively to the situation from C$_3$ to C$_6$, in these situations C$_6$ is more than half the length of C$_10$ and C$_10$ is more than half the length of C$_16$. This can be explained using the same arguments as above. From C$_6$ to C$_16$, the solubility of the alcohols in polystyrene decreases (at any particular temperature) and therefore on going from C$_6$ to C$_16$ the effects of polymer–solvent chemical affinity and stereochemical hindrance are both playing in the same direction, that is both hinder diffusion.

Table IV. Viscosity (mPa s) of the Alcohols in Their Liquid State ($T > T_m$) at Different Temperatures

Temperature (°C)	Viscosity (mPa s)						
	C$_1$	C$_2$	C$_3$	C$_4$	C$_6$	C$_10$	C$_16$
55	0.3790	0.6333	–	–	–	–	–
65	0.3432	0.5387	0.8308	1.038	–	–	–
75	–	0.4613	0.6846	0.8550	1.235	2.399	–
85	–	–	0.5671	0.7087	1.022	1.898	–
95	–	–	0.4717	0.5897	0.8465	1.533	3.110
105	–	–	–	0.4913	0.7100	1.260	2.466
115	–	–	–	0.4086	0.6027	1.053	1.990
125	–	–	–	–	–	0.8940	1.632
135	–	–	–	–	–	–	1.358
145	–	–	–	–	–	–	1.145

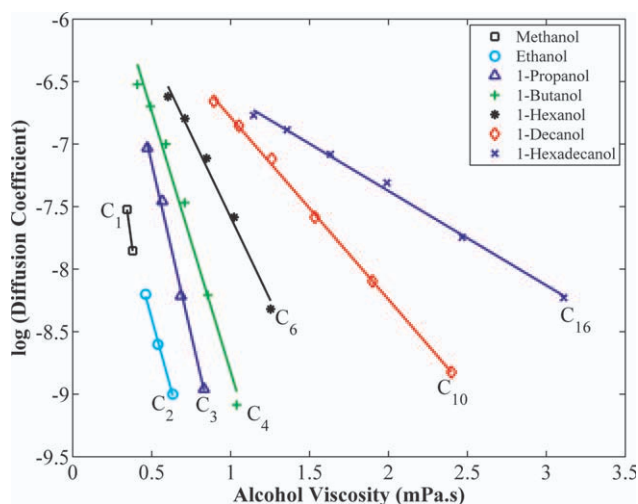**Figure 4.** Diffusion coefficients (cm^2 s^{-1}) for alcohols in polystyrene as a function of the alcohol viscosity: ($\square$) methanol (C1), (O) ethanol (C2), ($\triangle$) 1-propanol (C3), (+) 1-butanol (C4), (*) 1-hexanol (C6), ($\diamondsuit$) 1-decanol (C10), and (X) 1-hexadecanol (C16). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In the following discussion, an attempt is performed to correlate the diffusion coefficients obtained with several different physical parameters.

Following from the suggestion of previous authors,[40–42] the dependence of log D on the viscosity of the liquid penetrants has also been tested. The viscosity of the alcohols at different temperatures, as taken from Daubert et al.,[55] is listed in Table IV. Figure 4 shows the dependence of log D on the viscosity of the alcohols. As shown in Figure 4, for all the liquid penetrants, log D decreases linearly when the viscosity of the liquid increases. This linearity is very good as evidenced by the values of the corresponding correlation coefficients R^2 obtained, which were C$_2$ (0.9928), C$_3$ (0.9946), C$_4$ (0.9818), C$_6$ (0.9860), C$_{10}$ (0.9988), and C$_{16}$ (0.9953). The author is well aware that this type of correlation, as the one shown in Figure 4, can be sometimes misleading owing to the fact that temperature changes are also implicit in the change of viscosity. One of the major problems in this kind of studies lies precisely in the great difficulty of deconvoluting the effects of different experimental variables such as temperature, solvent viscosity, and polymer–solvent interaction parameter (χ). Therefore, at the moment, the linearity relationship shown in Figure 4 is just an empirical observation which is corroborated by the fact that similar linear relationships between the log D and the *solvent viscosity* are also observed in the diffusion of other homologous series of organic compounds (namely, linear 1-carboxylic acids[50] and linear alkanes[51]) into polystyrene, which suggests the general applicability of this relationship.

Attempts have also been performed to correlate the diffusion coefficients obtained with other previously suggested parameters (number of carbon atoms (n), solvent molecular weight M_w) using some previously suggested correlations (log D versus n; log D versus log M_w). However, and contrary to what

has been observed in the diffusion of n-alkanes in polystyrene,[51] in the case of the diffusion of alcohols in polystyrene the results obtained with any of these correlations were not satisfactory and for this reason they are not displayed here. Interestingly, Ward and coworkers[46,47] on their studies of the liquid diffusion of n-alkanes[46] and esters[47] through a thermoset adhesive have also found that the relationship "log D = log b + a log M_w" could describe successfully the diffusion coefficients of alkanes but not the diffusion coefficients of esters, according to the authors owing to the specific chemical interactions involving the esters. In the particular case of the diffusion of alcohols reported in the present study, one possible explanation for the breaking down of the power law relationship is the extensive hydrogen bonding and associated clustering which is known to occur in liquid alcohols. This phenomenon has been extensively documented in the literature in several different kinds of systems, namely: (i) in alcohols in their pure liquid state[56,57]; (ii) in alcohols mixed with small molecules such as ethylbenzene,[58] which may be considered an approximate small-molecule analogue of polystyrene; and (iii) in the sorption of alcohols into polymer membranes such as polyimide[59] and poly(dimethylsiloxane).[60] Alcohols have the ability to form multiple hydrogen bonds and to cluster through their hydroxyl groups. On the other hand, the alkyl groups of the alcohol molecules exclude potential partners from hydrogen bonding and therefore the larger these alkyl groups the smaller the average number of molecules per cluster. This, well documented, decrease of the average number of molecules per cluster with the increase in alkyl chain length may help explain the similar diffusivities observed for the alcohols C3, C4, and C6 (Figure 3) if it is assumed that, for example, cluster sizes of four molecules may be favored for C3, three molecules for C4, and two molecules for C6. However, this is just a hypothesis which lacks a strong experimental support. It is worth mentioning that despite the fact that hydrogen bonding and clustering in liquid alcohols have been known for many decades, a deep fundamental understanding of these highly complex systems is still lacking as it is attested by the continuous efforts that are still being performed on this very specific research topic.[56,57]

CONCLUSIONS

The rates of polystyrene swelling in linear alcohols (C$_n$, with n = 1, 2, 3, 4, 6, 10, and 16) as well as the diffusion coefficients of the same linear alcohols in polystyrene have been determined over a broad temperature range, using the mass uptake method. For all the alcohols considered, the mass uptake curves as a function of $t^{1/2}$ conform to a Fickian diffusion mechanism.

For each liquid penetrant, over all the temperature intervals considered, its diffusion coefficients were found to correlate very well with the corresponding liquid viscosities through a linear relationship of the type: log D proportional to *viscosity*. This supports similar relationships observed on the diffusion of linear carboxylic acids[50] and n-alkanes[51] on polystyrene.

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