Molecular sorption mechanism of solvent diffusion in polymers

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Abstract

Some experimental results from the literature are difficult to explain by the existing diffusion theories using a concentration gradient or a swelling rate. A new diffusion mechanism is proposed, in which the driving force for diffusion is the sorption of penetrant molecules onto polymer chains. Resistance of the matrix to the flow of penetrant opposes this force. Both forces are a direct consequence of molecular interactions. The interaction between the solvent molecules can be expressed by viscosity η and by surface tension T_s. The interaction of solvent with polymer matrix can be described by wettability (or contact angle α). The molecular structure of the polymer and its density fluctuations (average capillary radius r) are also important. Swelling of the matrix will change the molecular geometry and thus solubility. The rate of diffusion can be expressed as $v = (T_s/4\eta)r\cos\alpha \ 1/(x_0 + B)$ and the diffusion distance as $x_0 = B((kt + 1)^{1/2} - 1)$, where B and k are diffusion constants. The concentration dependence on distance and time is well described by an empirical equation $C/C_0 = \exp(-(x/x_0)^{ax_0})$, where constant a describes the sharpness of the diffusion front.

This model is applicable to swelling or non-swelling polymers, gels and porous media and can so far explain all the observed features of the diffusion process. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The observation of a sharp diffusion front [1,2], followed by a constant concentration has shown that the Fickian diffusion theory [3] is not directly applicable to polymers. This theory has been adapted from the diffusion of heat [4], and therefore assumes that all concentrations are equally probable. It also ignores the unrealistically high diffusion rates at the initial stages [5]. There have been many attempts to modify the Fickian mechanism in order to explain the observed concentration profiles. Most of the effort has been put into theoretical work, as accumulation of reliable and accurate experimental data is difficult. The concentration dependent diffusion coefficient [6] can only partially explain the observed sharp diffusion front. The mechanism of moving boundaries [7] is based on the assumption that two substantially different diffusion coefficients describe the diffusion in swollen and un-swollen regions. The diffusion coefficient changes abruptly in the narrow front region, providing a steep concentration gradient. The approach can explain the observed sharp diffusion front and has lead to the development of Case II mechanism [8–10]. The rate of diffusion in Case II mechanism is assumed to be controlled by osmotic pressure, acting against the creep viscosity of the swelling polymer in a narrow region of the diffusion front. The diffusion rate is therefore predicted to be constant, as some scientists have observed [11–12]. A concentration gradient is still needed for molecular transport in the swollen region. In order to explain a nearly constant concentration, it is assumed that there is an insignificant resistance to flow of the penetrant, i.e. a very high diffusion coefficient.

There are however several experimental observations which the above mechanisms cannot explain. Some of these have already been discussed in the literature and are briefly summarised below.

2. Experimental observations

Any successful mechanism of solvent diffusion in polymers, must explain at least the experimental observations of the following features: sharp diffusion front and constant concentration in the diffused layer [13–15], the observed diffusion rate [5,16], accumulation of penetrant in cavities or voids [16,17] and permeability rate directly related to the diffusion rate and solubility [18].

2.1. The rate of diffusion

The differences between two major diffusion mechanisms

(Fickian and Case II) are the concentration profiles and the rate of diffusion $v = \mathrm{d}x_0/\mathrm{d}t$. The diffusion distance for the Fickian mechanism follows a function $x_0 = at^{1/2}$, while for the Case II it follows $x_0 = bt$, (where a and b are constants for the best fit to experimental data). Accurate measurements (e.g. of methanol diffusion in polystyrene [16] or PET [19]) however show that none of the above mechanisms or their combination ($x_0 = at^{1/2} + bt$) can explain the measured data. It has been concluded in [5], that a finite rate of diffusion at the initial stages of diffusion process and a resistance of the polymer matrix to the flow of penetrant can explain the measured diffusion rates very accurately. These simple and logical requirements should therefore be incorporated into all diffusion mechanisms.

2.2. Constant solubility

Concentration gradient driven mechanisms require a large range of equally possible concentrations and are therefore not applicable to systems with only one thermodynamically advantaged solubility. The experimental observations, using numerous analytical techniques [13–15,17,20], indicate that the concentration following the diffusion front is constant within the accuracy of experimental error. Even if we assume that there is a concentration gradient, it will be very small. In order to maintain the diffusion rate for a small concentration gradient the diffusion coefficient for the swollen region must be very high. This presents a contradiction for observed permeability.

2.3. Permeability

The explanation of the observed concentration profile has been based on an assumption of two different states of polymer matrix. In the non-swollen region the diffusion is slow and a steep concentration gradient is formed. This is followed by an easy diffusion through the swollen region, with a high diffusion coefficient. A small concentration gradient is required to maintain the flow, as the diffusion is controlled by the slow diffusion in the diffusion front. The calculated and the observed concentration profiles are in the first approximation similar. However, when the diffusion front reaches the outer surface of the membrane, the whole membrane is swollen and only one diffusion coefficient controls the permeability. This is the case for Fickian diffusion. The extraction of the permeant from the surface will reduce the surface concentration and a high concentration gradient will be established. This would result in a very high permeability, which is not experimentally observed. A different explanation of the concentration profile is therefore needed.

2.4. Filling up voids

Voids in the polymer can be filled up by the penetrant. This has been demonstrated on PS/methanol system [16] using light microscopy observation and on epoxy/acetic acid-water system using nuclear magnetic resonance imaging (MRI) [17]. This means that mass transport can occur from 100% concentration to low concentration as well as from low concentration to a 100% concentration. This effect cannot be explained by a concentration gradient or by phase separation. Phase transition requires a substantial change in solubility (molecular interaction) with temperature and also some mass transport, but it is a different process than isothermal diffusion. Osmosis also has to be excluded, as the concentration of the penetrant inside the void and outside the polymer has been found by NMR/MRI [17] to be identical for different water/acetic acid mixtures. No permselectivity, required for osmosis, has been observed and filling up of voids also occurs for monomolecular penetrants [16]. Similar effect to void filling is the condensation of penetrant on the other side of the membrane, when not removed by evaporation or washed out. This clearly shows that pure penetrant and the swollen polymer are two coexisting equilibrium states. The properties of the penetrant molecules, the polymer matrix molecules and the polymer/penetrant mixture must therefore be all taken into account.

3. Diffusion mechanism of molecular sorption

It has long been recognised (mainly by those working with filtration membranes and by biologists), that polymers on a microscale are not homogeneous materials. The density fluctuation in a matrix with randomly arranged polymer chains is between two extremes: crystalline density and an empty space. Computer simulation and experimental measurements indicate that the spatial distribution of density fluctuation is on a nm scale, providing therefore sufficient 'porosity' for sorption and permeability of small molecules, even without swelling or molecular dynamics. The inhomogeneity of diffusion in the amorphous phase has been demonstrated e.g. by electron microscopy [14] and often an assumption of 'diffusion channels' is made in order to explain some permeability effects in filtration membranes [18]. The porosity has been investigated e.g. by position lifetime spectroscopy [21] and has shown pores of about 0.3 nm average diameter. In addition, polymers can swell relatively easily by absorbing a solvent. In this respect polymers behave like a porous medium, where the driving force for diffusion is molecular interaction, resulting in an internal pressure, similar to capillary pressure observed on a macroscale.

The molecular interaction between the solvent molecules can be expressed as surface tension T_s. Interaction with the wall of a capillary tube of a radius r (Fig. 1) can be measured by a contact angle α. The resulting pressure can therefore be
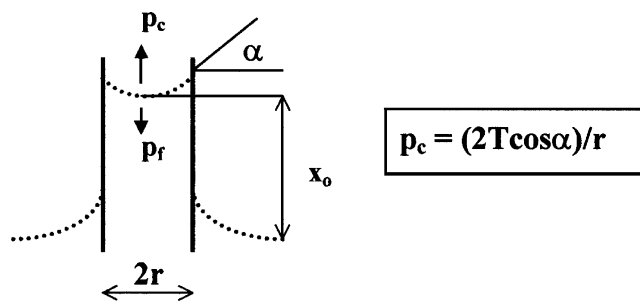
$$p_c = (2T\cos\alpha)/r$$

Fig. 1. Schematic diagram showing the molecular interaction parameters responsible for capillary pressure. When applied to polymers, the capillary radius represents an 'average' space between the molecular chains.

expressed as

$$p_c = (2T_s \cos\alpha)/r$$

The capillary pressure is opposed by the resistance to flow (Fig. 2). Poiseuille's equation describes the pressure needed for the flow of a liquid with viscosity η through a capillary of radius r, length l and at rate v as:

$$p_f = (v8\eta l)/r^2$$

For a flow of liquid the pressure needed to maintain velocity v must be supplied by a capillary pressure, i.e. $p_c = p_f$. The resistance to flow will change with the advancement of the diffusion front and the tube length l will be replaced by a variable diffusion distance x_0. The rate of flow v thus will be:

$$v = dx_0/dt = 2T_s \cos\alpha\, r^2/8\eta x_0 r$$

This can be rearranged in a more convenient form as

$$v = (T_s/4\eta)\,(\cos\alpha)\, r\,(1/x_0) \tag{1}$$

The first term, $T_s/4\eta$ represents the molecular interaction between the liquid penetrant molecules. Both are measurable parameters and can be correlated with others, such as vapour pressure.

The second term, $\cos\alpha$ represents interaction between liquid penetrant molecules and the molecules of the polymer matrix. This contact angle (or wettability) can be measured with some success, but it would be difficult to replace it by another parameter. It represents sorption of molecules by the polymer and together with surface tension T_s is the major driving force for diffusion in this mechanism.
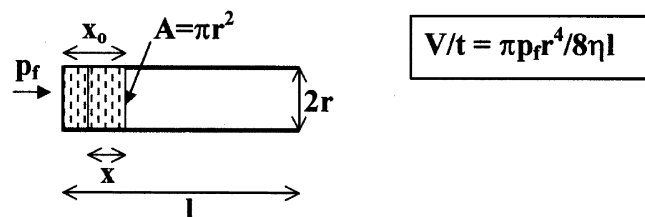

$$V/t = \pi p_f r^4/8\eta l$$

Fig. 2. Schematic diagram for Poiseuille's equation, representing resistance to flow of a liquid through a tube. For polymers the size of the capillary tube varies along the diffusion path.

The third term, r represents average size of inter-connecting pores (or capillaries). The pores are opened further by capillary forces to a level, which corresponds to an equilibrium with the uncoiling of the polymer chains (solubility level). This swelling process can only be in the direction perpendicular to the diffusion front, as in the direction parallel to the diffusion interface the surrounding material also swells. The resulting anisotropy can be visualised in polarised light.

The fourth term, $1/x_0$ describes the dependence of the diffusion rate on the distance of the diffusion front from the polymer/liquid interface. This is of practical interest in order to evaluate the time dependence and permeability. We can therefore consider the first three terms as a constant A for a given polymer system and temperature. The rate of diffusion must be finite at the very beginning of diffusion, which can be achieved by assuming that the diffusion starts at a given distance B (see Fig. 3). It is also convenient for simplicity of calculation to assume that the constant $A = B^2 k/2$, where k is a constant. The rate of diffusion thus will be:

$$v = B^2 k/2(x_0 + B) = dx_0/dt \tag{2}$$

The diffusion distance x_0 can be calculated from Eq. (2) by separating the variables and integrating:

$$\int B^2 k\, dt = \int 2(x_0 + B)\, dx_0$$

$$B^2 kt = (B + x_0)^2 + C$$

The integration constant C for boundary conditions $t = 0$ and $x_0 = 0$ is $-B^2$ and therefore

$$x_0 = B((kt + 1)^{1/2} - 1) \tag{3}$$

It has been shown previously [5] that this equation can explain the experimental data very accurately. This is shown in Fig. 4, where the measured distance penetrated by methanol in PMMA is plotted as the square root of time. The intercept with the y axis is $-B$, the intercept with the x axis is $1/k^{1/2}$ and the slope of the straight line is $Bk^{1/2}$. Both constants are therefore measurable.

The concentration profile of the above mechanism has a sharp diffusion front and for a homogeneous matrix a constant concentration in the penetrated layer. It is possible that in some systems the concentration will increase further with time, causing some residual swelling. The concentration profile can be calculated from the mass conservation equation:

$$v(dm/dx) = d(s + m)/dt$$

where m is the mobile mass and s is the mass sorbed on to the matrix molecules. The solution to this equation is cumbersome and in-practical. It can be replaced by a simple empirical equation, which describes the concentration
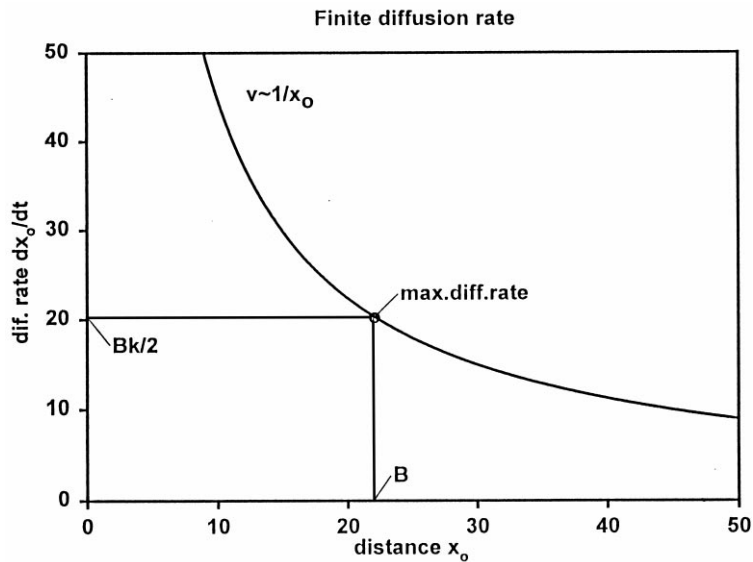
Finite diffusion rate

Fig. 3. The rate of diffusion dependence on the diffusion distance x_0 (or $t^{-1/2}$). The limited velocity at the beginning is equivalent to a starting point at distance $x_0 = B$.

profile very well:

$$c/c_0 = \exp(-(x/x_0)^{ax_0}) \qquad (4)$$

where c_0 is solubility and a is a constant, describing how steep the diffusion front is. Fig. 5 shows the calculated profiles for different values of a. Fig. 6 shows the good fit of this equation to data obtained by MRI [17].

4. Discussion

The mechanism of molecular sorption assumes, that molecular interaction between the polymer chains and the penetrant is attractive. There are very few cases when this interaction is repulsive. An example is PTFE, which, although highly porous, will not allow water to diffuse into or through it. The interaction is dependent on functional groups of both compounds and will to some extent vary from region to region, depending on the orientation and 'clustering' of these groups. The detailed nature of molecular cohesive forces can only be speculated [22], but the general opinion is that dispersive forces play a major role. The general value of the cohesive forces can be estimated by using thermodynamics [23] for internal pressure, which for
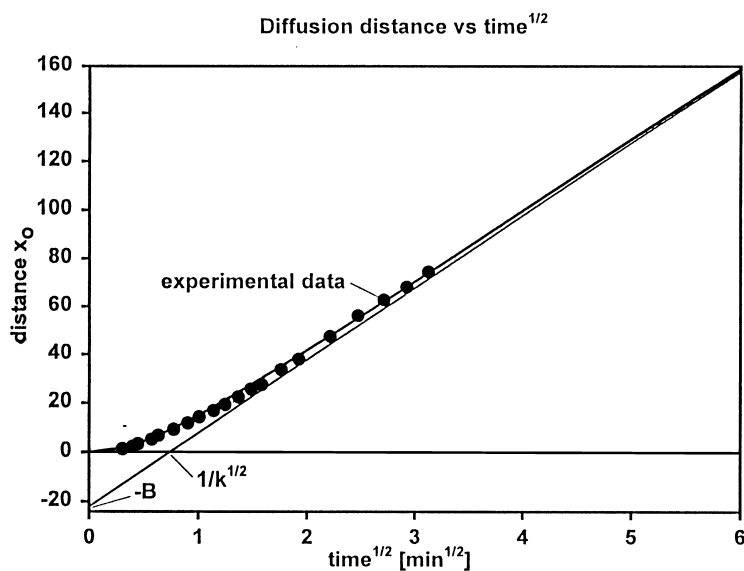
Diffusion distance vs time$^{1/2}$

Fig. 4. Graph of diffusion distance (in μm) versus square root of time with experimental data ($\bullet$) fitted to the equation $x_0 = B((kt + 1)^{1/2} - 1)$. A straight line extrapolated to data at large distances (for $kt \gg 1$, $x_0 = B(kt)^{1/2} - B$) intercepts the x and y axis at points corresponding to diffusion constants $1/k^{1/2}$ and $-B$, respectively.

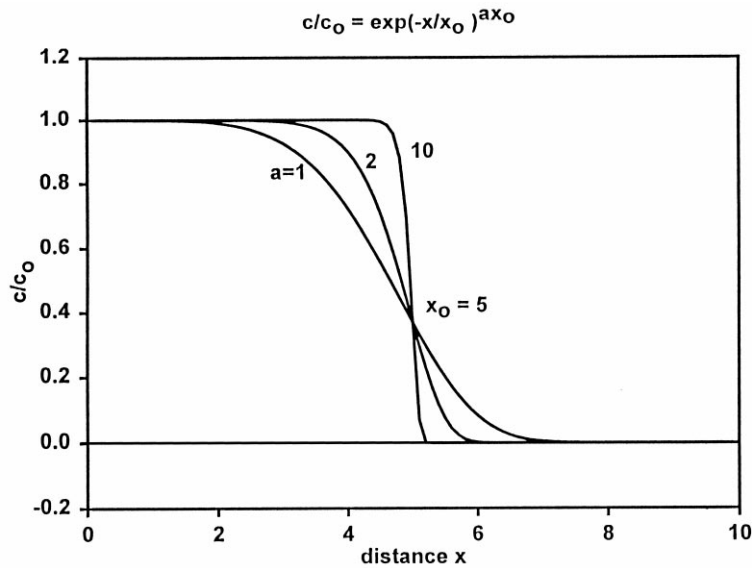$$c/c_O = \exp(-x/x_O)^{ax_O}$$

Fig. 5. Concentration profiles calculated from Eq. (4) for different values of a constant 'a'. The slope of the concentration transition at the diffusion front, can be selected.

most compounds has values in the order of 3000 atm (water has a value of 20 000 atm). This might explain why a 20 μm thick polymer film, sandwiched firmly between two 0.5 mm thick glass slides, can fracture the glass when exposed to a solvent.

It can be assumed that forces between dissimilar molecules will be different, most probably lower. This is clearly manifested by observed filling of voids [16,17]. Here the molecular attraction between the penetrant molecules is greater than between the penetrant molecules and the polymer functional groups. When penetrant molecules diffuse to the surface of a void, they attract each other and form a liquid, filling up the space. The gas or air present in the

void will be compressed and absorbed by the penetrant and/or by the swollen polymer matrix. The filling of voids is a clear violation of the concentration gradient principle and shows that concentration gradient driven mechanisms are not applicable for diffusion of solvents into polymers.

A constant concentration throughout the entire penetrated region indicates that a thermodynamic equilibrium has been reached. When the supply of penetrant is discontinued, the concentration remains unchanged and the diffusion front also remains sharp, providing that the penetrant is not removed by evaporation. This shows that the forces trying to reach the equilibrium solubility are much greater than the forces trying to reduce the concentration gradient. Therefore
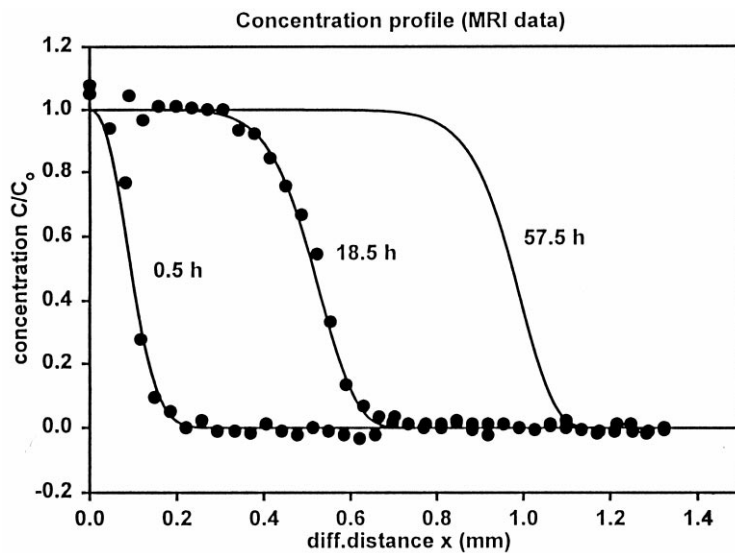

Fig. 6. The best fit to the MRI data from [17] for 0.5 and 18.5 h of immersion of epoxy in acetic acid. The concentration profile for 57.5 h is predicted. The MRI data have not been corrected for resolution or distortion.

the concentration gradient is clearly not the driving force for diffusion when one concentration is thermodynamically advantaged, in which case a phase diagram can be established.

The concentration profile at the diffusion front is difficult to measure. The spatial resolution, thickness correction, contrast width, use of contrast enhancers etc. are rarely considered and uncorrected data are presented in the literature. In addition the concentration variation can occur as a result of the polymer matrix inhomogeneity. When the rate of diffusion is higher in some regions than in others an average concentration will show a broad front transition. For a homogeneous matrix, the front should be very sharp, as the molecular forces between penetrant molecules are high and will not allow a gradient to be established. It is difficult to study the geometry of diffusion on a microscale or in 3D but it might be obvious that similarly to any fibrous material the low density regions will have continuity, but more theoretical and microscopical investigation is needed.

The $t^{1/2}$ dependence of the diffusion distance means that the diffusion rate is controlled by the resistance to flow. The resistance to flow is dependent on the viscosity of the penetrant, on the size of open pores and on the distance from the polymer surface. Diffusion rate is also influenced by the attractive forces of the matrix and by the external pressure. It may be possible in the future to predict the values of diffusion, solubility and permeability for a given system, using the above parameters. A comprehensive experimental and theoretical study of various aspects of this mechanism is in progress.

5. Conclusions

An alternative mechanism of diffusion is proposed, that does not require a concentration gradient as a driving force. It is based on molecular interactions between all components and can so far explain all the observed effects of mass transport. In particular, it can explain logically a constant concentration and a sharp diffusion front, the relationship between permeability and diffusion rate, filling of pores and the behaviour of multiple penetrants. Experimental evidences show that polymers behave like a porous medium, with pores on a molecular scale. This mechanism opens new possibilities in the effort to identify parameters which control the diffusion processes. The important and measurable parameters for diffusion are viscosity and surface tension of the penetrant, contact angle between the penetrant and the polymer and density and density fluctuation of the polymer matrix. Alternatively, the rate of diffu-

sion in a particular polymer/solvent system can be described by two measurable, temperature dependent constants 'B' and 'k'. The third possible description of the principles outlined here is thermodynamics, using parameters such as chemical potentials, partial pressures, entropies and enthalpies of mixing etc. These will be particularly useful for evaluation of solubility levels and polymer swelling equilibria, but unfortunately practical theories are yet to be developed. The most popular (and successful) Flory–Huggins approximation cannot unfortunately take into account a specific molecular structure. More promising are some new emerging theories, e.g. the Polymer Reference Interaction Site Model [24], or similar. A thermodynamical approach is now being considered, but because of the complexity of the treatment it will take some time to develop. It will inevitably introduce parameters, which are more difficult to obtain and verify than the parameters used here, but it might provide a better understanding of the fundamental principles of diffusion and miscibility, hopefully justifying some assumptions made here.

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