The effect of stirring on the diffusion of small molecules from a polymer matrix into a solution

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The probability for small molecules to travel between two points in space under diffusion and stirring in a time t is determined and used to find the amount of mass transferred from a polymer matrix into solution. Both diffusion and stirring govern the behaviour of the migrants; diffusion depends on the mean value of the diffusion coefficient and stirring forces the particles to move in a specific manner. The results of g.c. experiments, measuring the number of dioctylphthalate plasticizer molecules diffusing from the matrix of a poly(vinyl chloride) film into an oil solvent, with and without stirring, confirm the theoretical relationships.

(Keywords: stirring; diffusion; plasticizers)

INTRODUCTION

The description of the diffusion of low molecular weight species in a matrix is of fundamental importance due to its numerous applications. The diffusion of charged particles due to a hopping motion in various materials is a first example of the capability of the phenomenon to describe the conductivity and other macroscopic properties of these substances[1–4]. The same phenomenon also finds application in the field of drugs and other bioactive products[5–7], since these species must be released at a controlled rate usually from a polymer matrix in which they are initially dispersed. A third field where the diffusion of molecules is important is in the construction of polymeric containers for foodstuffs, and pharmaceutical and medicinal products. Additives, such as plasticizers, stabilizers, antioxidants and lubricants, used to improve the mechanical, chemical and physical properties of the packaging materials may diffuse from the plastic into the solid or liquid contacting media and contaminate them[8–13]. Another important reason for the study of the macroscopic behaviour of the diffusants is that it is strongly related to the state of the matrix in which they diffuse and analytical monitoring of the diffusion may be employed for the study of the matrix itself[14,15]. The description of both static and dynamic macroscopic behaviour of polymer matrices can be pursued in this way and changes of behaviour have been detected by means of measuring diffusion coefficients[16,17].

Both experimental and theoretical methods have been employed to study the diffusion of migrants through polymer matrices. The experimental methods used include holographic grating techniques which use the monitoring of the signals from the diffusants induced by forced Rayleigh scattering or laser beams[16–19]. Gas chromatographic analysis[8–10] of properly derivatized samples also provides a high degree of precision in the measurement of the quantities of diffusants transferred into specific regions, such as of a solution in contact with a solid matrix. Theoretical efforts to describe phenomena related to the diffusion of the migrants in a polymer matrix include free volume theories[18–22], according to which the diffusing penetrant molecules advance through the available free volume of the matrix with various degrees of difficulty. Monte Carlo[5] simulations and analytical solutions based on Smolocouwki's[23] and Fick's[24,25] diffusion equations have also been employed. The diffusion of low molecular weight compounds can also be described by means of random walks and from this point of view the trajectory of a diffusing particle is like the configuration of a polymer chain, the length of which plays the role of time[26–28]. In this way, a polymer matrix consisting of polymer chains can be studied. The trajectory path of the diffusing particle is then like a fictitious chain in the presence of other real chains. Special interactions may be included in this sense between the chains which amend the description of the phenomenon beyond that of free diffusion. In more concentrated systems of migrants, interactions between them may also be incorporated[29,30].

In this paper we study the diffusion of migrants giving the solution of the initial free diffusion problem in terms of the probability of migration of a diffusant between two points in space. In this solution many effects can be incorporated like those from specific interactions or confinement of the motion of the diffusants. An example of the capability of incorporation of further effects is given by studying in detail the effects from stirring[31] which causes an extra organized motion of the diffusants. A comparison of theoretical with experimental results is also presented.

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THE PROPAGATOR

The diffusion of particles in a matrix can be studied by means of the differential equation (Fick's second law):

$$\frac{\vartheta C}{\vartheta t} - D\nabla_R^2 C = 0 \tag{1}$$

which describes the concentration $C(R, t)$ of the particles at any point R and time t in terms[24,25] of an effective diffusion coefficient D. In order for $C(R, t)$ to describe specific systems proper boundary conditions have to be applied to the general solution of the differential equation. It is known for example that the solution which describes free diffusion of mass M of particles which are gathered initially at the point $R_0 = 0$ is given by:

$$C(R, t) = \frac{M}{8(\pi D t)^{3/2}} \exp(-R^2/4Dt) \tag{2}$$

More difficult examples describe the diffusion in specific geometries or under specific interactions and most of the time cumbersome boundary conditions are difficult to apply[24,25,32–34].

For the description of some systems it is more convenient to use a correlated quantity, namely, the probability $P(R_0, R; t)$ of a particle starting from the point R_0 to be at the point R in time t, which obeys a similar differential equation[26–28]:

$$\frac{\vartheta P}{\vartheta t} - D\nabla_R^2 P = \delta(R - R_0)\delta(t) \tag{3}$$

The Dirac delta functions $\delta(R - R_0)$ and $\delta(t)$ of equation (3) vanish everywhere except at $R = R_0$ and $t = 0$ and specify R_0 to be the starting point of the motion. The diffusion equation is separable along the three cartesian axis and the propagator P is a product of three independent components along the three perpendicular directions:

$$P = P_x P_y P_z \qquad \text{where all } P_i = \frac{1}{2\sqrt{\pi D t}} \exp\left[-\frac{(i - i_0)^2}{4Dt}\right] \qquad (i = x, y, z) \tag{4}$$

It is normalized with respect to integration over all space ensuring the fact that the migrants have to be somewhere in space at any time. Having the form of $P(R_0, R; t)$ problems like the evaluation of mass transfer at specific intervals of time from specific parts of space to other parts of space can at once be solved by integration of $P(R_0, R; t)$ for the time interval and the space variables involved, respectively. The propagator P is of a fundamental nature and can be employed for the detailed study of the motion of the diffusants by finding, for example, their mean displacements as a function of time or the frequency of visiting specific sites in the sample. Describing mass transfer by means of the probability P, equation (4), has some advantages compared to the solution of the initial differential equation for $C(R, t)$ because the first avoids the cumbersome boundary conditions necessary for the description of special systems by means of the second method. P as the solution of equation (3) can also be expressed by means of path integrals[26–28] and it is of special interest when diffusion takes place in a polymeric matrix since the real chains can also be described by path integrals, about which many studies have been carried out. The trajectories of migrants will be like fictitious polymer chains where the molecular weight proportional to the length of the chain is equivalent to time.

Equation (3) describes an initial problem. Other effects like those resulting from specific interactions between the migrants and the matrix or the confinement in specific geometries can be incorporated. We present here an example of the incorporation of organized motion by means of stirring. The particles beyond their free diffusion are also forced to move by mass flow in a certain manner and direction. If the particles are moving with an extra average velocity u towards the positive z direction only the z component of P will be affected and those of the free diffusion along the x and y directions will remain the same. A term equal to the product of the velocity u and the gradient $\vartheta P/\vartheta z$ along the this direction has to be included[35–38] and the solution of the three-dimensional problem including stirring is equivalent to the solution of the differential equation:

$$\frac{\vartheta P}{\vartheta t} - D\nabla_R^2 P - u\frac{\vartheta P}{\vartheta z} = \delta(R_0 - R)\delta(t) \tag{5}$$

P is a function of the components of the vector $R_0 - R$ and the solution of equation (5) will describe the diffusion of particles under stirring. It can easily be solved in the combined Fourier and Laplace spaces as far as the space and time variables are concerned, respectively. Defining:

$$\bar{\bar{P}}(k, s) = \int_{-\infty}^{\infty} \mathrm{d}R \exp[-i(R - R_0)k] \int_0^{\infty} \mathrm{d}t \exp(-st) P(R - R_0; t) \tag{6}$$

as the combined Fourier and Laplace transform of P, equation (5) becomes $(s + Dk^2 - uik_z)\bar{\bar{P}}(k, s) = 1$ which yields for $\bar{\bar{P}}(k, s)$ the expression:

$$\bar{\bar{P}}(k, s) = \frac{1}{s + Dk^2 - uik_z} \tag{7}$$

P can then be found from equation (7) by inverse Laplace and Fourier transforms and equals:

$$P = \frac{1}{8(\pi D t)^{3/2}} \exp\left[-\frac{(x - x_0)^2 + (y - y_0)^2 + (z - z_0 - ut)^2}{4Dt}\right] \tag{8}$$

New features dependent on the value of the velocity u along the z direction change the z dependence of P from that of equation (4). It becomes a Gaussian moving in the z direction with velocity u. Knowing the form of P, quantities like the mean square displacement of the migrants or the amount of mass transfer from a specific sample to the solution with stirring $(u > 0)$ or without $(u = 0)$ can be determined.

THE AMOUNT OF MASS TRANSFERRED INTO SOLUTION

An important quantity is the amount of mass transferred into solution and can easily be determined by means of accurate experimental methods like gas[8–10] or liquid[39,40] chromatography, mass spectrometry[11], spectrophotometry[41] or Raman spectroscopy[42] and radioactivity[43,44] or radio trace analysis[45,46]. We will determine this quantity in terms of D, u and t and the characteristics of the sample. We consider that our solid matrix has a width λ adjusted along the negative z direction and a perpendicular surface S at the $z=0$ plane. The migrating molecules which are initially uniformly spread throughout the whole matrix diffuse under stirring and a percentage of them go into solution in the positive subspace, $z>0$. In order to find the amount of mass M_t of migrants which transfer into solution as a function of the time t we have to integrate x_0, y_0 and z_0 to cover all possible initial positions of the molecules in the matrix and x, y, z to cover their final positions lying everywhere in the positive space where the solution is:

$$M_t=C'\int_S^{\infty}\mathrm{d}x_0\int_S^{\infty}\mathrm{d}y_0\int_{-\lambda}^{0}\mathrm{d}z_0\int_S^{\infty}\mathrm{d}x\int_S^{\infty}\mathrm{d}y\int_0^{\infty}\mathrm{d}zP \tag{9}$$

where the x and y integrations are performed over the total available surface of escape S and C' is a constant proportional to the total mass of migrants. If we divide by M_∞ the total mass of migrant which under stirring diffuses finally ($t\rightarrow\infty$) into the solution we can get rid of C' and obtain the expression:

$$M_t/M_\infty=\frac{ut}{2\lambda}\operatorname{erf}\left(\frac{ut}{2\sqrt{Dt}}\right)+\frac{ut-\lambda}{2\lambda}\operatorname{erf}\left(\frac{\lambda-ut}{2\sqrt{Dt}}\right)$$
$$+\frac{\sqrt{Dt}}{\lambda\sqrt{\pi}}\left\{\exp\left[-\frac{(ut)^2}{4Dt}\right]-\exp\left[-\frac{(\lambda-ut)^2}{4Dt}\right]\right\}+\frac{1}{2} \tag{10}$$

Trivial checks on the final form of M_t are in order. What we obtain from this equation are some interesting limits. For $t\rightarrow 0$ the limit $M_t/M_\infty=\sqrt{Dt}/\lambda\sqrt{\pi}$ is obtained, and its dependence on $\sqrt{Dt}$ is in accord with previous results where diffusion mainly without stirring has been studied. What we notice is that this limit is independent of u which means that M_t/M_∞ increases with $\sqrt{Dt}$ in the small time limit regardless of whether stirring is included or not. For larger times the two cases differentiate and two different limits are obtained as $t\rightarrow\infty$ depending on whether we have stirring or not. Without stirring $M_t/M_\infty\rightarrow 1/2$ meaning that the free diffusion keeps on average half of the molecules in the negative region $z<0$. For $u>0$ the limit M_t/M_∞ goes to 1 expressing the fact that all mass under organized motion finally ends at the positive subspace $z>0$. Graphs based on equation (10) and without stirring are shown in *Figures 1–3*.

From the general expression of equation (10) describing both diffusion and stirring, the two separate phenomena of pure diffusion ($u=0$) and pure stirring ($D=0$) can be studied:

$$M_t/M_\infty=\frac{1}{2}-\frac{1}{2}\operatorname{erf}\left(\frac{\lambda}{2\sqrt{Dt}}\right)+\frac{\sqrt{Dt}}{\lambda\sqrt{\pi}}\left[1-\exp\left(-\frac{\lambda^2}{4Dt}\right)\right]$$

pure diffusion ($u=0$) (11a)

$$\begin{aligned} M_t/M_\infty &= ut/\lambda \text{ for } t<\lambda/u \quad \text{pure stirring} \quad (D=0)\\ &=1 \quad\ \text{ for } t>\lambda/u \end{aligned} \tag{11b}$$

These equations are plotted in *Figure 4*. Notice that when stirring is dominant a linear dependence of M_t on t is taken in accordance with previous results[31]. In the case of pure diffusion, equation (11a), in the limit of small times M_t/M_∞ depends on $\sqrt{Dt}$ and goes as that out of a slab[47–50]. The dependence of M_t on λ, determined to

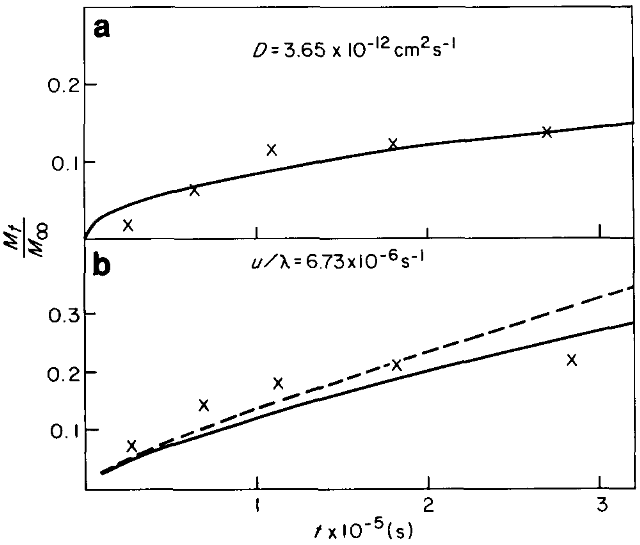

Figure 1 Least square fitting curves: (a) without stirring, equation (11a); (b) with stirring, equation (10), at 6°C. The solid line corresponds to $u/\lambda=6.73\times10^{-6}\,\mathrm{s}^{-1}$, found by minimizing the sum of the squares of the differences between the experimental values of M_t/M_∞ and those of equation (10). The dotted line corresponds to $u/\lambda=9.35\times10^{-6}\,\mathrm{s}^{-1}$, found by minimizing the sum of the simple differences between the experimental values of M_t/M_∞ and those of equation (10)

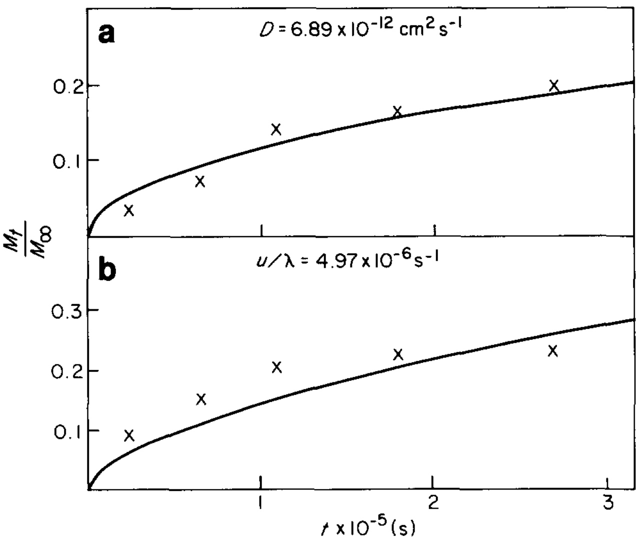

Figure 2 Least square fitting curves: (a) without stirring, equation (11a); (b) with stirring, equation (10), at 22°C

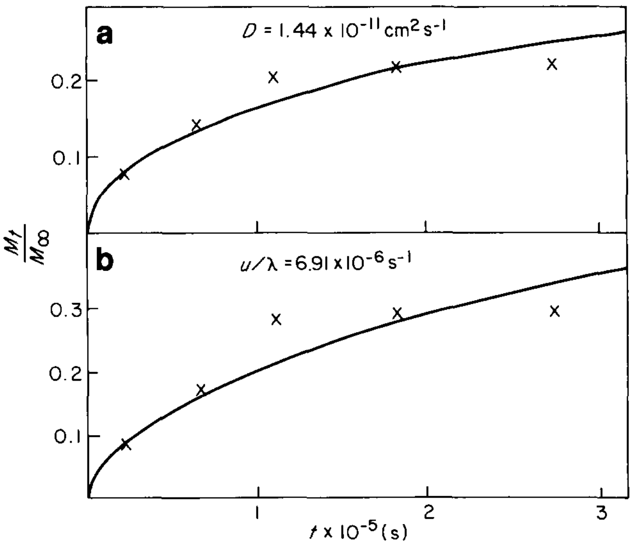

Figure 3 Least square fitting curves: (a) without stirring, equation (11a); (b) with stirring, equation (10), at 30°C

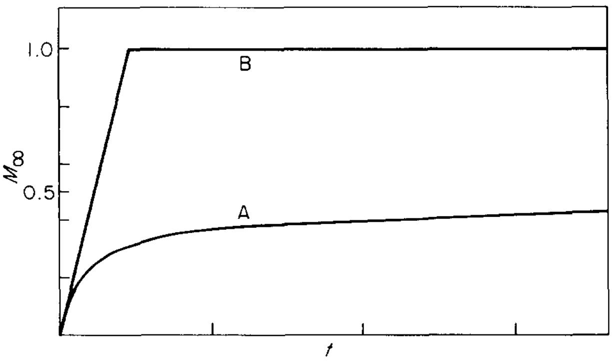

Figure 4 From the general solution of equation (10), the two separate phenomena of pure diffusion and pure stirring can be described: (A) pure diffusion ($u=0$), equation (11a); (B) pure stirring ($D=0$), equation (11b)

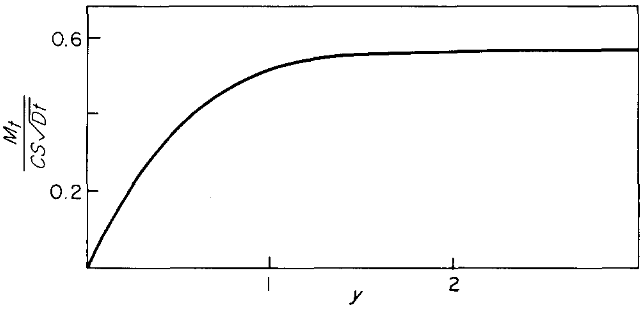

Figure 5 Dependence of mass transfer on the reduced parameter y

be linear initially and ending with a plateau[51,52], is also given by equation (11a). If we substitute $M_\infty = CS\lambda$ in equation (11a), where C is the total available concentration of the diffusants in the initial sample and S the total surface of escape, we obtain:

$$\frac{M_t}{CS\sqrt{Dt}} = y\left\{1-\mathrm{erf}(y)+\frac{1}{y\sqrt{\pi}}[1-\exp(-y^2)]\right\} \qquad (12)$$

where $y=\lambda/2\sqrt{Dt}$ is a reduced variable. The plot of this function is shown in *Figure 5* and is of the same form as that of previous studies[51,52]

COMPARISON OF THEORETICAL RESULTS WITH THOSE OBTAINED EXPERIMENTALLY BY GAS CHROMATOGRAPHY

Equation (10) is a general expression describing the mass M_t transferred into solution as a function of time t, the stirring velocity u, the diffusion coefficient D and the sample width λ. The last three parameters appear in the two combinations D/λ^2 and u/λ. Experiments have been carried out by measuring M_t of the dioctylphthalate plasticizer from a poly(vinyl chloride) matrix into an oil solvent as a function of time t, with and without stirring. Gas chromatography measurements were carried out at three different temperatures (6, 22 and 30°C) and *Table 1* shows the results obtained with stirring ($u>0$) and without stirring ($u=0$). Equation (11a) depends on the single parameter D/λ^2 and can be employed for the determination of the value of this parameter for each temperature. The condition we choose for this purpose is the minimization of the sum of the squares of the differences of the experimental values of M_t/M_∞ and those taken from equation (11a). All these least square curves are shown in *Figures 1–3*; the values of D found after multiplying D/λ^2 by λ^2 ($\lambda = 1.27 \times 10^{-3}$ cm) are shown in the figures. It is seen that all these single parameter graphs fit well with the experimental results. The dependence of D on temperature is an increasing function of temperature in accordance with previous results[53]. The values of D of the present work lying in the range between 10^{-11} cm s^{-2} and 10^{-12} cm s^{-2} are generally smaller than those of previous references[43,44,53,54] and this is due to the presence of the oil solvent being more viscous than the solvents used in those studies. From the experimental pairs (M_t/M_∞, t) with stirring and knowing the diffusion parameters D/λ^2 the stirring parameters u/λ can also be determined by means of equation (10) which thus remains to include only the parameter u/λ. By means again of the condition of minimization of the sum of the squares of the differences between the experimental and theoretical values of M_t/M_∞ the parameter u/λ can be determined for each temperature. The three different theoretical curves for the three different temperatures are shown in *Figures 1b*, *2b* and *3b*; the values for u/λ are shown in the figures. Though this choice of theoretical curves is not unique, the fact that the sum of the squares of the differences between the experimental and theoretical values is a minimum keeps the shapes of the theoretical curves the closest possible to the shapes of hypothetical experimental curves which join the experimental points. Again a good fitting is taken between theory and experiments providing a measure of the mass transfer velocity of the order of $u \sim 10^{-8}$ cm s^{-1}.

Table 1 Experimental values of M_t/M_∞ at various time intervals without and with stirring

$t \times 10^{-5}$ (s)	M_t/M_∞					
	Without stirring			With stirring		
	6°C	22°C	30°C	6°C	22°C	30°C
0.216	0.018	0.032	0.078	0.078	0.093	0.086
0.648	0.063	0.071	0.143	0.142	0.150	0.174
1.080	0.111	0.138	0.202	0.182	0.203	0.279
1.800	0.118	0.163	0.219	0.203	0.217	0.291
2.700	0.130	0.191	0.221	0.204	0.218	0.296

CONCLUSIONS

A theoretical equation of the probability of a migrant to travel in time t between two points in space with and without stirring is determined and used to find the amount M_t of low molecular weight compounds which pass from a polymer matrix into a solution as a function of the time t.

The function M_t/M_∞ depends on two parameters; the diffusion parameter D/λ^2 and the stirring parameter u/λ. For short times, M_t/M_∞ goes as $\sqrt{Dt}$ with or without stirring and when stirring is dominant a linear dependence of M_t/M_∞ on ut is taken. Without stirring, half of the available quantity of migrants diffuses in the positive solution region yielding the limit $\underset{t\to\infty}{M_t/M_\infty} = 1/2$ while under stirring all of the available migrants end in solution so that the limit $\underset{t\to\infty}{M_t/M_\infty}$ goes to 1.

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