Notes to the Editor

Calculation of diffusion coefficients of organic vapours from short and longtime sorption data

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Much work is reported in the literature about the sorption of organic vapours in polymer films. In typical sorption experiments the mass gained by a sample held in the vapour atmosphere at constant temperature and pressure is followed with time. In many situations these curves are initially linear. Under these circumstances the diffusion coefficient is related to the mass gain by the following equation

$$M_t/M_\infty = (2/\pi^{1/2})(Dt/l^2)^{1/2} \tag{1}$$

where the thickness of the sheet is $2l$. If the diffusion coefficient is an increasing function of concentration, linearity continues until a higher value of M_t/M_∞ is achieved. It is common practice to use the initial slopes of these curves to obtain the value of the diffusion coefficient and its variation with the concentration of the diffusing substance.

The solution to the diffusion equation

$$\partial C/\partial t = D(\partial^2 C/\partial X^2)$$

for a case where sorption is taking place on a thin sheet of thickness $2l$, with constant concentration on the surfaces and constant D, leads to the following relationship[1]:

$$Y = (8/\pi^2)[\exp(-\beta t) + (1/9)\exp(-9\beta t)$$
$$+ (1/25)\exp(-\beta t) + \ldots] \tag{2}$$

where

$$\beta = D\pi^2/4l^2, \quad Y = (1 - M_t/M_\infty)$$

and the nth term in the series is given by

$$\exp(-(2n - 1)^2 \beta t)/(2n - 1)^2$$

At large values of time the difference between the sum of the entire series and the first term becomes insignificant, so that a plot of $\ln(Y)$ vs t shows a straight line. It should be possible to compute the diffusion coefficient from the limiting slope $-\beta$, of these plots. When this procedure is followed for systems known to have concentration dependent D, it is noticed that the plots show a clear break at a certain stage of sorption and the slope abruptly changes. Several systems reported in literature have been examined and found to exhibit this behaviour. A typical example is the sorption of benzene on PBMA reported by Machin and Rogers[2]. The

data are plotted in *Figure 1*. The original sorption curve has Fickian characteristics. Similar breaks on the $\ln(Y)$ vs t plots have been observed in the sorption of benzene in polyisobutylene[3] and acetone in PVAc[4].

A more interesting fact is that when $\ln(Y)$ vs t plots are constructed from sorption data of 'non-Fickian' systems, a similar break is observed in several cases. A good example of this is the sorption of acetone in cellulose acetate reported by Bagley and Long[5]. The plot is shown in *Figure 2*. Similar behaviour has been found in the sorption of methyl iodide in cellulose acetate[6] and methylene chloride in polystyrene[7].

For systems where the diffusion coefficient continuously varies with concentration, the slope of these semilog plots should not be constant with the progress of the sorption/desorption process. On this basis Chernova and Vasenin[8] suggested a method for the determination of the $D-c$ relationship from single desorption curves. In the cases cited above, however, the slope is constant with the progress of sorption until an appreciable quantity of the penetrant is sorbed. This feature, along with the appearance of the break in the semilog plots, seems to be characteristic of systems where the diffusion coefficient is very low at low concentrations, increases sharply beyond a certain concen-
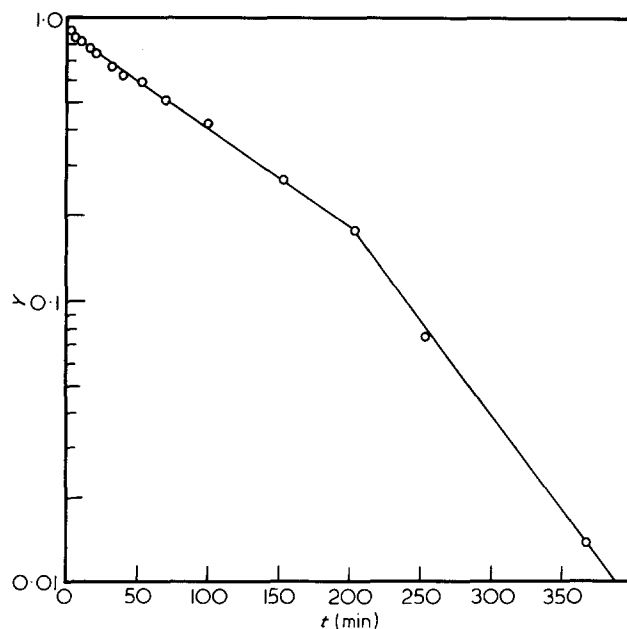
Figure 1   Sorption of benzene in PBMA, 23°C. Data: Machin and Rogers[2]
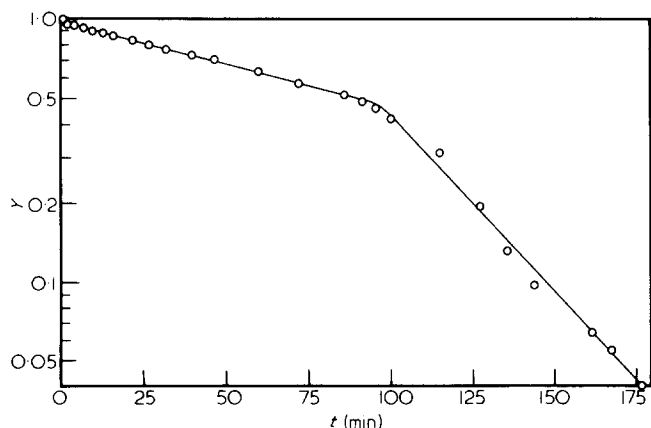
Figure 2 Sorption of acetone in cellulose acetate at $30°C$, thickness $= 4.0 \times 10^{-3}$ cm. $p_i = 0$ mm, $p_f = 120$ mm, Data: Bagley and Long[5]

tration to a much higher value. A limiting case will be one of a discontinuous diffusion coefficient which has been discussed by Crank[1]. The calculated concentration distance curves of these systems suggest that diffusion will take place with two 'advancing fronts' or moving boundaries in the sheet. These moving boundaries will eventually meet at a certain stage of sorption and soon after this event, sorption will be governed by a high value of the diffusion coefficient because the low concentration region in the sheet will quickly disappear. If the actual process is nearer this model, the effect of this event should be reflected on the sorption plots. The following analysis summarized from Crank[1] applies to this model and will be used to demonstrate the significance of the break mentioned above.

Consider a sheet extending in thickness between $x = 0$ and $x = 2l$. Let one of the advancing fronts be at a distance X from the sheet surface ($x = 0$) at time t and let the concentration in the region $0 < x < X$ be represented by C. C is then a function of x and t. Also if the diffusion coefficient rises from zero to D at $C = C_X$, then

$$C = C_X \text{ at } x = X \tag{3}$$

$$\partial C/\partial t = D(\partial^2 C/\partial x^2) \text{ in the region } 0 < x < X \tag{4}$$

$$C = C_0 \text{ at } x = 0 \text{ at } t \geqslant 0 \tag{5}$$

Before the advancing fronts meet at $t = t_0$ the medium is effectively semi-infinite and the solution of (4) satisfying (5) is

$$C = C_0 + A \text{erf}[x/2(Dt)^{1/2}] \tag{6}$$

where A is a constant.

Since the equation must be satisfied for all values of t, it follows that X must be proportional to $t^{1/2}$, i.e.

$$X = kt^{1/2} \tag{7}$$

where k is a constant.

Substituting (7) in (6) with the condition (3) we obtain,

$$C_X/C_0 = (A/C_0)\text{erf}(k/2D^{1/2}) + 1 \tag{8}$$

It can be further shown[1] that the quantities C_X/C_0 and $k/2D^{1/2}$ are related by the equation

$$C_X/C_0 = 1/(1 + \pi^{1/2}Q(\exp Q^2)\text{erf} Q) \tag{9}$$

where $Q = k/2D^{1/2}$.

From equations (8) and (9) it is apparent that there is only one independent variable between the three quantities C_X/C_0, A/C_0 and $k/2D^{1/2}$. For a chosen value of $k/2D^{1/2}$ therefore, the parameters C_X/C_0 and A/C_0 can be calculated.

The extent of sorption through a unit area of the half sheet (M_t) is easily obtained from the flux at $x = 0$. Differentiating equation (6) we get

$$\partial M_t/\partial t = -D(\partial C/\partial x)_{x=0} = -A(D/\pi t)^{1/2}$$

which on integration leads to

$$M_t = -2A(Dt/\pi)^{1/2}$$

At infinite time when the sheet has attained equilibrium and the concentration everywhere is C_0, $M_\infty = lC_0$. Thus

$$M_t/M_\infty = (-2A/C_0\pi^{1/2})(Dt/l^2)^{1/2} \tag{10}$$

For sorption, the constant A/C_0 should have a negative value. The initial sorption plot will be linear if M_t/M_∞ is plotted against $t^{1/2}$.

The slope on a plot of M_t/M_∞ vs $(Dt/l^2)^{1/2}$ should be $-2A(\pi^{1/2}C_0)$, constant till the advancing fronts meet. The later sorption period for which equation (10) is not valid, has been shown to follow the following equation[1]

$$M_t/M_\infty = 1 + 2\sum_{n=0}^{\infty} \exp[-D(2n+1)^2\pi^2(t-t_0)/4l^2] \times$$

$$\left\{ (2(-1)^n/(2n+1)\pi) \times \right.$$

$$\left. \int_0^1 (f(x)/C_0)\sin((2n+1)\pi x/2l)d(x/l) - 4/(2n+1)^2\pi^2 \right\}$$

$$\tag{11}$$

where

$$f(x)/C_0 = 1 + (A/C_0)\text{erf}[(x/l)/2(Dt_0/l^2)^{1/2}] \tag{12}$$

and from (7)

$$(Dt_0/l^2)^{1/2} = D^{1/2}/k \tag{13}$$

For plotting the theoretical sorption curve a value for $k/2D^{1/2}$ is chosen and the quantity A/C_0 is determined from equations (9) and (8) and finally the sorption curve is constructed using the equations (10) and (11). The integral in (11) is easily evaluated numerically with the help of (12) once $k/2D^{1/2}$ is chosen and A/C_0 is calculated.

Following this procedure starting with $k/2D^{1/2} = 0.4$, sorption points have been plotted on a semilog graph paper in *Figure 3* and in the usual form in *Figure 4*.

A break in the curve is clearly visible in *Figure 3* although *Figure 4* appears 'normal'. The similarity between the cal-

culated curve and the experimental one of Machin and Rogers is clearly visible. Similar calculations have been made by the author with $k/2D^{1/2}$ taken as 0.3, 0.48 and 0.61 and in each case the break is seen. The extent of departure of the slope should clearly depend on $-A/C_0$ which increases with increasing value of $k/2D^{1/2}$ eventually approaching unity when the system will behave strictly in accordance with equation 1. The calculated value of C_X/C_0 approaches zero under these conditions.

Although these results have been obtained from a model which assumes the limiting case of discontinuous diffusion coefficients which may not be fully describing a real case, the similarity between the theoretical and the experimental curves indicates that it very nearly represents the actual process. It follows that in a markedly concentration-dependent system there will be a rapid change in the gradient but not a discontinuous change from one straight line to another, when $\ln(1 - M_t/M_\infty)$ is plotted as a function of time. This is because in such a system a sharp 'moving front' will not exist. The 'front' will be somewhat diffused depending on the extent of concentration dependence. The rate of sorption which depends on $-D(\partial C/\partial x)$ at the outer surfaces of the sheet will take some time to react to the change occurring at the sheet centre.

We shall now examine the significance of this model as far as the value of D as determined from experiments is concerned. In common practice the value of D is calculated from the initial slope using equation (1). Comparing equa-

Figure 4 Calculated sorption curve with $k/2D^{1/2} = 0.4$

tion (1) with equation (10) it is clear that this value, will always be off by the factor $(A/C_0)^2$, compared to the diffusion coefficient corresponding to the highest concentration involved in the experiment. Thus, for the case analysed, with $k/2D^{1/2} = 0.4$, A/C_0 comes out to be −0.61. The diffusion coefficient calculated from equation (1) will be 0.37 times the real one in this case. *Table 1* gives the ratio of diffusion coefficients calculated from the slope after the break and equation (1), using data from three different authors.

The procedure for calculation of D based on equation (11) has a direct theoretical justification compared to use of equation (1) the basis for which is constant D throughout the concentration range. In equation (11) the summation term involves $(2n + 1)^2$ in the negative power of the exponential. The influence of terms for $n > 0$ will therefore be negligible. Thus if terms other than $n = 0$ are dropped, we have

$$(1 - M_t/M_\infty) = -2Z\exp[-D\pi^2(t - t_0)/4l^2]$$

where Z equals the quantity in curly brackets of equation (11). Calculations show that it is a negative quantity.

Taking logarithms and writing all constants collectively as $\ln K$ we get

$$\ln(1 - M_t/M_\infty) = \ln K - (D\pi^2/4l^2)t \tag{14}$$

The slope after the break will therefore be $-D\pi^2/4l^2$ from which D can easily be calculated.

Some authors[2,9,10,11] have in the past used the long time sorption data close to equilibrium for the calculation of D. The 'advancing front' model offers a rigorous justification for the same procedure. However it necessitates the use of factor $(A/C_0)^2$ if equation (1) is used for the calculation of D corresponding to highest concentration involved.

The phenomenon of break in sorption curves is to a great extent explained by the 'advancing fronts' model, which warrants further investigation.

Table 1

	Data Source	System	D_s/D
1	Machin and Rogers[2]	PBMA-Benzene, 23°C	0.38
2	Hayes and Park[3]	Polyisobutylene-Benzene, 25°C	0.45
3	Kokes et al[4]	PVAc-Acetone 20°C	0.55

D_s is the value calculated from equation 1
D is the value calculated from later slopes (after the break) on the $\ln(Y)$ vs t plot
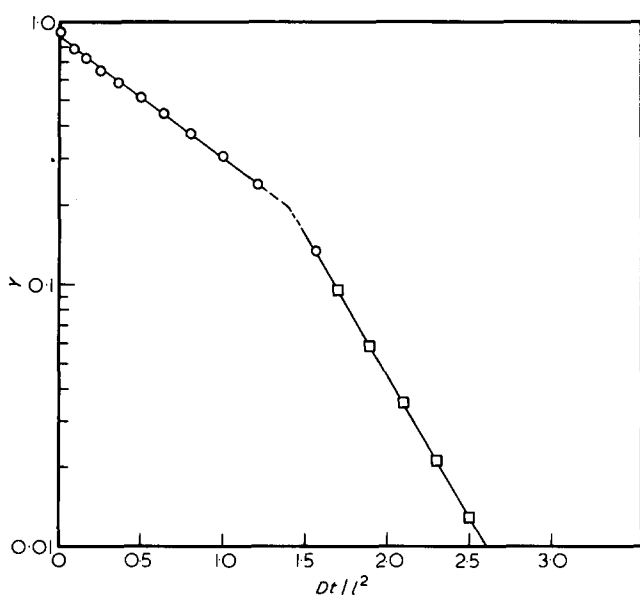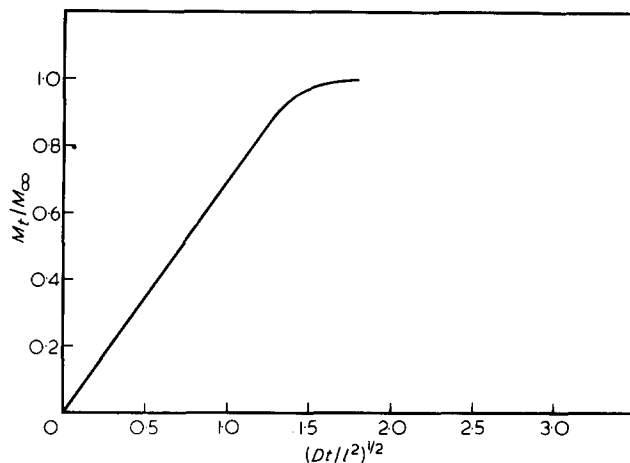

Figure 3 Calculated sorption behaviour with 'advancing fronts' $k/2D^{1/2} = 0.4$ —O— points calculated from equation (10); —□— points calculated from equation (11)

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Parameters affecting the onset of drag reduction in polymeric solution

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INTRODUCTION

Studies on the drag reduction phenomenon in polymeric solutions indicate the existence of a threshold level of shear stress which must be exceeded before the drag reduction manifests itself. This effect is known as the onset of drag reduction and is influenced by both 'flow' and 'polymeric' parameters. White[1], and Vleggaar, Dammers and Tels[2] found analytically that the Reynolds number corresponding to the inception of drag reduction is proportional to the pipe diameter raised to the power of 8/7. However, the results of these studies do not explain all the experimental results obtained with different polymers[3,4].

In the present note, the model due to Denn has been adapted to represent the viscoelastic properties of the drag-reducing fluid. Results obtained indicate that the onset Reynolds number is a function of the pipe diameter, the type of polymer and its concentration, as well as the velocity gradient near the wall. Experimental results available in the literature have been explained qualitatively using the present analysis. Further, it is shown that the result obtained by Vleggaar *et al.*[2] forms a particular case of the present study.

ANALYSIS

A drag-reducing fluid is considered as a viscoelastic one possessing the Newtonian viscosity. Such a fluid fits the Denn model[5], represented by the following rheological equation:

$$\tau^{ij} + \tau(\mathrm{II}/2)^{(s-2)/2} \frac{\delta \tau^{ij}}{\delta t} = 2\mu e^{ij} \tag{1}$$

where τ^{ij}, e^{ij} are the components of the deviatoric stress tensor and the rate of strain tensor, respectively. $\delta/\delta t$ represents the convected derivative and I is an invariant of e^{ij}.

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Further, μ, τ and s are material constants.

For one dimensional flow, equation (1) reduces to

$$\left[1 + \tau(\mathrm{II}/2)^{(s-2)/2} \frac{\mathrm{d}}{\mathrm{d}t} \right] \sigma(t) = \mu \frac{\mathrm{d}}{\mathrm{d}t} \gamma(t) \tag{2}$$

where $\bar{\tau}(\mathrm{II}/2)^{(s-2)/2}$ represents the relaxation time of the fluid related to the exponentail stress decay at a constant strain. II for established flow is $4(\mathrm{d}V_z/\mathrm{d}y)^2$, where V_z is the bulk flow velocity in z-direction. For periodic strain of the type

$$\gamma = \gamma_0 \exp(i\omega t)$$

the stationary solution of equation (2) is

$$\sigma(t) = \gamma_0 \frac{\mu}{\tau(1/2\mathrm{I})^{1/2(s-2)}} \left[\frac{i\omega\tau(\mathrm{II}/2)^{(s-2)/2}}{1 + i\omega\tau(\mathrm{II}/2)^{(s-2)/2}} \right] \times$$
$$\exp(i\omega t) \tag{3}$$

for $t \gg \tau(\mathrm{II}/2)^{(s-2)/2}$

Introducing the complex relation modulus

$$G^*(\omega) = G'(\omega) + iG''(\omega) = \sigma(t)/\gamma(t)$$

one obtains

$$G'(\omega) = G \left[\frac{\omega^2\tau^2(\mathrm{II}/2)^{(s-2)}}{1 + \omega^2\tau^2(\mathrm{II}/2)^{(s-2)}} \right]$$

$$G''(\omega) = G \left[\frac{\omega\tau(\mathrm{II}/2)^{(s-2)/2}}{1 + \omega^2\tau^2(\mathrm{II}/2)^{(s-2)}} \right]$$

$$G'(\omega)/G''(\omega) = \omega\tau(\mathrm{II}/2)^{(s-2)/2} \tag{4}$$

where

$$G = (\mu/\tau)(\mathrm{II}/2)^{(2-s)/2}$$