Influence of interfacial resistance on kinetics of sorption

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A model for sorption influenced by rate of transfer to the surface layer of polymeric sheets has been examined. The rate of uptake into the surface layer has been taken to be proportional to the degree of unsaturation of the surface layer. The predicted sorption behaviour has been compared with experimentally observed data which shows a reasonable agreement. A method for calculating diffusion coefficients has been demonstrated. It has been shown that sorption rates could be affected by factors like pressure of the penetrant in the vapour phase and the structure of the surface vis-à-vis that of the bulk. Extension of the model qualitatively, to systems with diffusion coefficients strongly dependent on concentration, indicates the possibility of larger uptake of the penetrant in thinner sheets in an initial time interval. This supports some experimental observations reported earlier. The model supports the experimental work of Long and Richman who observed the time dependence of surface concentrations during sorption.

INTRODUCTION

Sorption of organic vapours in polymer films has been the subject of investigation by a large number of workers[1]. The results of transient experiments are correlated to give the diffusion coefficients[2]. In the initial period of sorption, the mass gain is related to time by the following equation:

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

where the thickness of the sheet is $2l$. Use of this equation involves the assumption that the surface of the sheet instantly attains equilibrium with the surroundings and the diffusion coefficient remains constant throughout the range of study in a single experiment.

In many situations it has been observed that sorption does not follow equation (1) and shows a non linear behaviour in the initial stages. This departure has been attributed to a variety of reasons such as time dependent diffusion coefficients, effect of internal stresses and time dependent surface concentrations.

Long and Richman[3] presented strong experimental evidence for time dependence of surface concentrations in the sorption of methyl iodide in cellulose acetate. What actually causes the delay in concentration build up in the surface has not been conclusively established. The mechanism discussed below offers some promise as will be clear from experimental evidence cited in this paper.

The transport mechanism at the solid gas interface must necessarily involve the transfer of molecules to the surface from the gas phase forming the adsorbed phase on the surface. The rate of adsorption at any instant should be proportional to the vapour activity (i.e. the ratio between the actual pressure of the penetrant to the saturation vapour pressure) and the fraction of vacant sites on the surface[4]. Hence:

$$\text{Rate of adsorption} = K_A(p/p_0)(1-\theta) \tag{2a}$$

θ is the fraction of sites occupied on the surface and K_A is the proportionality constant which depends on the system.

For mutually compatible adsorbent adsorbate pairs involving non rigid substrate, an adsorbed molecule will be indistinguishable from those lying dissolved in the surface layer of the chain segments[5]. The quantity θ can be replaced by the ratio C_s/C_e, where C_s is the concentration in the surface and C_e is the equilibrium concentration. Thus,

$$\text{Rate of adsorption} = k(C_e - C_s) \quad \text{where } k = K_A(p/p_0)/C_e \tag{2b}$$

Considering this transfer rate from gas phase per unit area of the interface, it follows that:

$$k(C_e - C_s) = -D(\partial C/\partial x) \tag{3}$$

since $-D(\partial C/\partial x)$ is the flux at the surface following Fick's law. Equation (3) is mathematically equivalent to the 'surface evaporation condition' discussed by Crank (reference 2, equation 3.34). Solutions similar to those given by Crank and earlier workers can be used in this case as well.

The solution of the diffusion equation $\partial C/\partial t = D(\partial^2 C/\partial x^2)$ under conditions defined by equation (3) on the two surfaces is,

$$\frac{C - C_2}{C_e - C_2} = 1 - \sum_{n=1}^{\infty} \frac{2L \cos(\beta_n x/l) \exp(-\beta_n^2 Dt/l^2)}{(\beta_n^2 + L^2 + L) \cos \beta_n} \tag{4}$$

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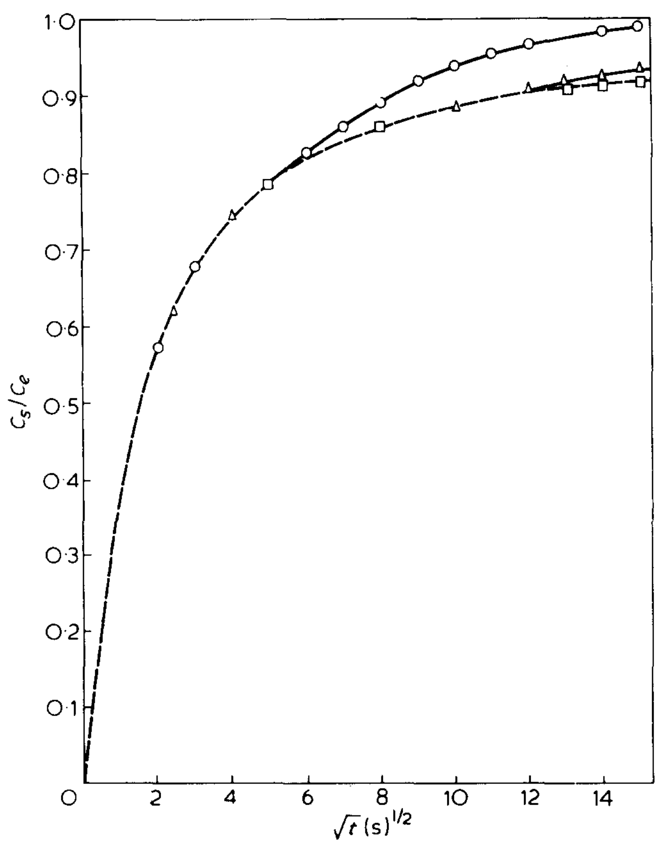

Figure 1 Variation of surface concentration with time for sheets of different thicknesses compared to semi-infinite solid. ○, L = 5, l = 0.001 cm; △, L = 10, l = 0.002 cm; □, L = 15, l = 0.003 cm; broken line = semi infinite solid; k/D = 5000

where β_ns are the positive roots of the equation:

$$\beta \tan \beta = L; \quad L = lk/D$$

If a sheet has zero concentration of the diffusant to start with, the surface concentration is given by:

$$\frac{C_s}{C_e} = 1 - \sum_{n=1}^{\infty} \frac{2L}{(\beta_n^2 + L^2 + L)} \exp(-\beta_n^2 Dt/l^2) \tag{5}$$

The fractional surface concentration C_s/C_e is plotted as a function of time in *Figure 1* for different values of L. The fractional mass gain obtained from equation (4) is given by

$$M_t/M_\infty = 1 - \sum_{n=1}^{\infty} \frac{2L^2}{\beta_n^2(\beta_n^2 + L^2 + L)} \exp(-\beta_n^2 Dt/l^2) \tag{6}$$

Using equation (6) the values of fractional mass gain can be plotted as a funtion of dimensionless parameters Dt/l^2 and L. A careful examination of these curves reveals that a linear region can always be located on the curve with high values of L. The slopes of these lines on the curves are identical (*Figure 2*). Curves of this shape have been reported in literature and the best example appears to be sorption of methylene chloride in polystyrene at 25°C[6]. Sorption curves with 35, 87 and 315μm thickness run parallel to each other in close agreement with the shapes of the calculated curves of *Figure 2*, which indicates that the process of sorption is controlled by some fundamental property of the system.

During the initial period of sorption the sheet is effectively semi-infinite, since the concentration at the sheet centre will be negligible. Solution of the diffusion equation for semi-infinite solids therefore will be useful in understanding the significance of the linear region in the calculated and experimental sorption curves. The solution of diffusion equation under condition (3) for semi-infinite solid is[2]

$$(C - C_2)/(C_e - C_2) = \operatorname{erfc}(x/2\sqrt{(Dt)}) - \exp(hx + X^2)\operatorname{erfc}((x/2\sqrt{(Dt)}) + X) \tag{7}$$

where $h = k/D$ and $X = h\sqrt{(Dt)}$

For the special case of zero concentration in the medium initially ($C_2 = 0$), the surface concentration ($C_s = 0$) is given by

$$C_s/C_e = 1 - \exp(X^2)\operatorname{erfc}(X) \tag{8}$$

The mass sorbed per unit surface is obtained from (7)

$$M_t = C_e(\exp(X^2)\operatorname{erfc}(X) - 1 + 2X/\sqrt{\pi})/h \tag{9}$$

This equation can be applied to sorption during the initial period till the sheet is effectively semi-infinite. It may be noted that the term $\exp(X^2)\operatorname{erfc}(X)$ will approach a negligible value compared to unity at higher values of X With progress of time, X becomes large enough so that the slope of the curve calculated from (9) remains steady at $2/\sqrt{\pi}$ when $M_t h/C_e$ is plotted as a function of $h\sqrt{(Dt)}$. (see

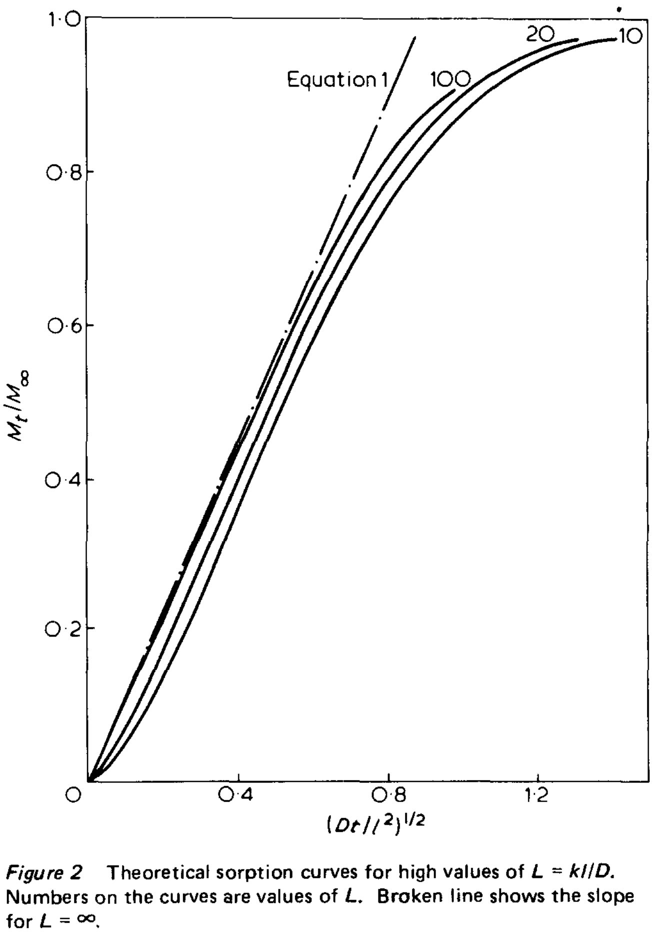

Figure 2 Theoretical sorption curves for high values of L = kl/D. Numbers on the curves are values of L. Broken line shows the slope for L = ∞.

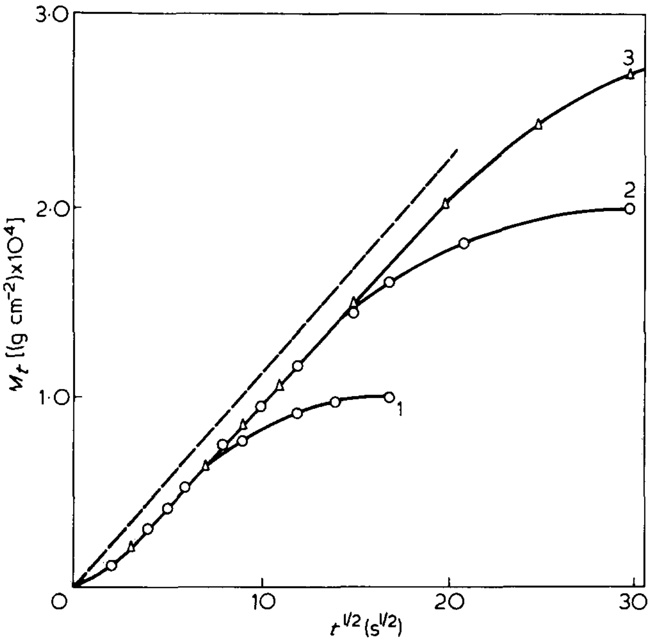

Figure 3a Theoretical mass gain as a function of time (equation 6). Half thicknesses are 0.001, 0.002, 0.003 cm for curves 1, 2 and 3 respectively. h = 5000 cm^{-1} and D = 10^{-8} cm^2 s^{-1}. Broken line is for h = ∞

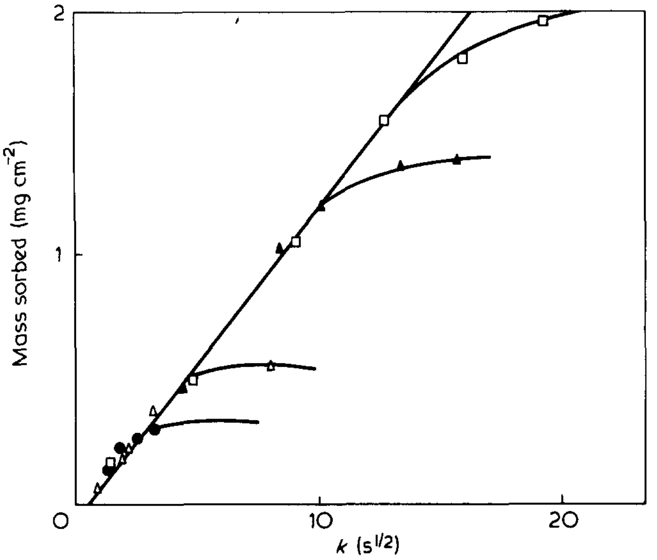

Figure 3b Sorption of methylene chloride in polystyrene, data: Park (Ref. 6). Sheet thickness: □, 315μ; ▲, 221μ; △, 87μ; ●, 47μ

Figure 3.5 of reference (2)).

Systems with relatively large value of $h\sqrt{D}$ will follow the following equation at large values of time

$$M_t = 2C_e(Dt/\pi)^{1/2} - \frac{C_e}{h} \qquad (10)$$

For a sheet with thickness $2l$ we can substitute C_e by M_∞/l and $(kl/D) = L$, to get,

$$M_t/M_\infty = \frac{2}{\sqrt{\pi}}(Dt/l^2)^{1/2} - \frac{1}{L} \qquad (11)$$

Equation (11) permits the calculation of D from the slope of the linear region. If fractional mass gain is plotted against $\sqrt{t}/l$ and the slope is s, the diffusion coefficient is given by $D = \pi s^2/4$. The quantity L can be calculated from the intercept on the ordinate. The procedure should, however, be used with caution, bearing in mind that it applies to systems with large value of L. It is interesting to note that for extremely large values of L, equation (11) reduces to equation (1).

If the mass gain by sheets of different thicknesses is calculated as function of $t^{1/2}$ using equation (6), the resulting curves are found to coincide in the initial region (*Figure 3a*). This is also a logical conclusion from equation (9). It is expected, therefore, that a system following the mathematical formulations discussed above should exhibit features of *Figures 1*, *2* and *3*. Such data can be analysed for the value of the physical constants such as the diffusion coefficient.

EXPERIMENTAL EVIDENCE AND DISCUSSION

Methylene chloride–polystyrene

Data reported by Park[6] on sorption of methylene chloride on polystyrene is shown in *Figure 3b*. The agreement with the form of theoretical plots of *Figure 3a* can be easily observed. From the slope of the line drawn through coinciding region, the diffusion coefficient works out to be 7.85×10^{-5} mm^2 ksec^{-1} or 7.85×10^{-10} cm^2 sec^{-1}. For this calculation C_e was estimated from the mass sorbed at equilibrium, per unit volume of the sheet with 0.087 mm thickness. Equation (10) was then used for calculating the diffusion coefficient. The same value of diffusion coefficient is obtainable from the steady slopes of curves with 0.035, 0.087 and 0.315 mm thickness on M_t/M_∞ vs. $\sqrt{t}/2l$ plot reported by the author. The validity of the surface resistance model was further tested on the sorption of methylene chloride in polystyrene at 25°C by comparing the position of experimental points with those calculated by using equation (9) in the initial sorption period. The calculated points agree fairly well with the experimental data for sorption well above $M_t/M_\infty = 0.5$.

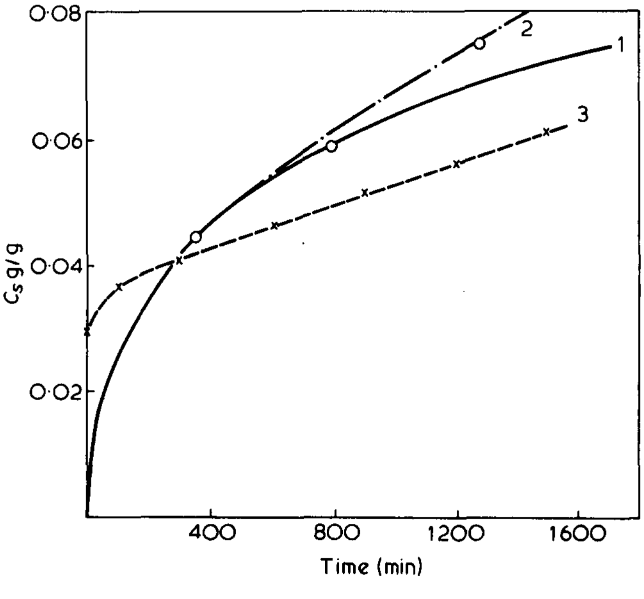

Figure 4 Time dependent surface concentration (1) is a plot of equation (8) (semi-infinite solid) with $h\sqrt{D}$ = 0.017. (2) Is the calculated curve for sheet with thickness 0.013 cm, h = 103, D = 2.74 x 10^{-8} cm^2 min^{-1}. (3) Is a plot of $C_S = C_e - (C_e - C_0)\exp(-Bt)$ for B = 1.66 x 10^{-4} and C_0 = 0.035, used by Long and Richman. ○, experimental points reported by Long and Richman

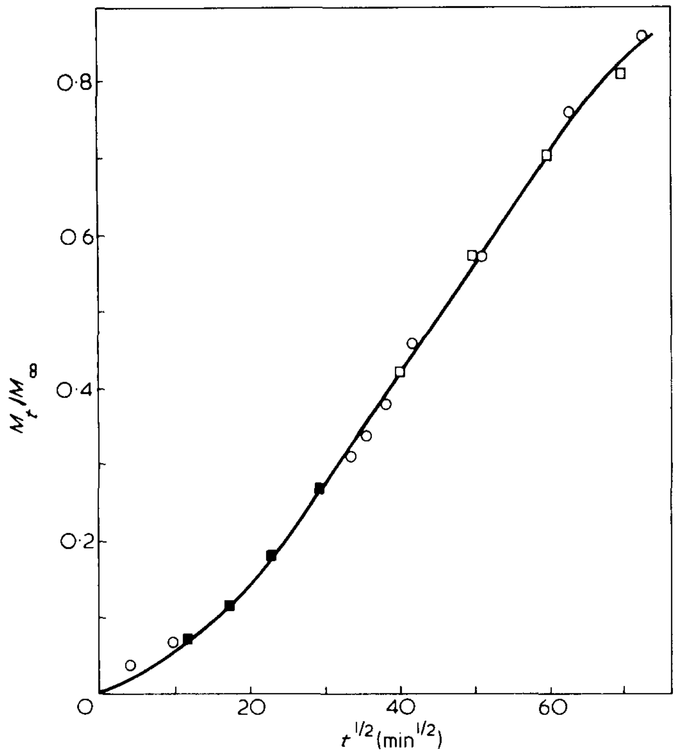

Figure 5 Test of surface resistance model in sorption of methyl iodide (200 mm) on cellulose acetate film of thickness 0.013 cm. ■; □, points calculated by using equations (9) and (6) with $h\sqrt{D}$ = 0.017 and L = 0.667; ○, experimental points reported by Long and Richman

Methyl iodide–cellulose acetate

In their study of sorption of methyl iodide into dry cellulose acetate, Long and Richman[3] measured the variation of surface concentrations using the microradiographic technique. They plotted the concentration profiles in sheets of thickness 0.009 to 0.013 cm exposed to vapours of methyl iodide at 200 mm at 40°C. The concentration on the surface increased with time and the concentration at the sheet centre remained negligible for a considerable length of time. The surface concentration–time data reported by these authors when used in equation (8) yields a value of $h\sqrt{D} = 0.017$. *Figure 4* shows the reported experimental values with the theoretical curves for a semi-infinite solid for $h\sqrt{D} = 0.017$ and for a sheet with thickness 0.013 cm. The agreement between the theoretical and the experimental values is good. It should be noted that the surface resistance model predicts that the surface concentration will be a function of the diffusion coefficient as well as the film thickness (equation 5).

In their paper, Long and Richman have proposed the surface concentration variation as $C_s = C_e - (C_e - C_o)e^{-Bt}$, independent of D and l. They have used a value of $C_o = 0.035$ and $B = 1.66 \times 10^{-4}\ \text{min}^{-1}$ for fitting the sorption data. Variation of the surface concentration according to this equation is also shown in *Figure 4*. The better fit of the surface resistance model is evident.

With the value of $h\sqrt{D}$ determined from the reported surface concentration, the sorption curve could be calculated by using equations (9) and (6). A value of $L = 0.667$ and $h\sqrt{D} = 0.017$ fits the experimental data remarkably well. These values lead to $D = 2.74 \times 10^{-8}\ \text{cm}^2\ \text{min}^{-1}$. *Figure 5* shows close agreement between theoretical and experimental points till $M_t/M_\infty = 0.8$. Deviation in the later sorption period could be attributed to an increase in the diffusion coefficient with concentration since, by that time the entire solid has a notable concentration of the diffusant molecules.

From the discussion in these paragraphs it can be concluded that if surface resistance is significant, the resulting sorption curves will be of a non-Fickian type. The diffusion coefficient can however be estimated from the linear portions of the sorption curves on thick sheets of polymer. The following points are important in this connection:

(a) If the polymer sheet used for experiment is such that the surface resistance is high compared to that of the bulk (this may be true in extremely thin sheets), the concentration of the diffusing species will acquire a notable value in the sheet centre before linearity sets in on the M_t vs. $\sqrt{t}$ graph. In such a case the results will have to be ignored. Experiment on thicker sheet for the same system under identical conditions should reveal the linear region.

(b) The constant 'h' has been taken to be independent of the sheet thickness in all the calculations for construction of *Figures 1, 2* and *3*. This constant is, by definition, the ratio between k and the diffusion coefficient D,

$$h = k/D = (p/p_oC_e)(K_A/D)$$

If sorption is taking place in a region where the sorption isotherm (i.e. equilibrium concentration vs. p/p_o curve) is non-linear the ratio p/p_0C_e will stand altered with pressure of the penetrant in the vapour phase, This will affect 'h' and hence the rate of soprtion as well.

The ratio K_A/D compared the natures of the surface in relation to a basic transport property of the bulk, i.e. the diffusion coefficient 'D'. One of the factors that may affect these values could be the history of formation of the sheet particularly if the solid involved is glassy. If the sheet is formed by the evaporation of a solvent from a thick solution, the surface layer is formed by rapid removal of the solvent whereas the interior loses the solvent slowly. The effect should be more pronounced in thicker sheets. The variation of 'h' with the thickness of the sheet is therefore a possibility, under certain conditions of sheet formation. A consequence of this factor could be that a thicker sheet offers relatively higher resistance at the

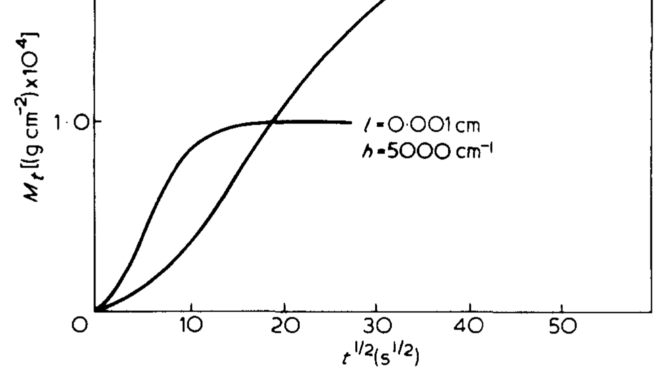

Figure 6 Effect of surface resistance and thickness on sorption. Calculated curves for $D = 10^{-8}\ \text{cm}^2\ \text{s}^{-1}$

surface i.e. the value of 'h' is lower for the thicker sheet. *Figure 6* shows the calculated curves for such a case. It can be seen that thinner sheets can absorb larger quantities than thicker sheets in the same interval of time under certain conditions. This effect has been experimentally observed by Park[6] in the sorption of methylene chloride in cellulose acetate. Such effects could also result partly due to factors discussed under (c) below.

(c) Complications will arise if the diffusion coefficient is an increasing function of concentration as has already been observed in many polymer diffusant systems. No direct solution of such a problem appears to have been worked out. However, it would be expected that systems with a substantial increase in 'D' with concentration, exhibit linearity till a higher value of M_t is attained, as is observed in 'Fickian' systems.

CONCLUSION

It is evident that non-Fickian characteristics can result from slow transfer to the surface layer. Some of the observed features of anomalous sorption can be explained with the help of this model.

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