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Analysis of Dual Diffusion and Non-linear Adsorption Isotherm with a Time Lag Method

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Abstract. This paper presents an application of the time lag method in the analysis of an adsorption system, where dual diffusion mechanism is assumed to exist and the equilibrium relationship between the fluid and adsorbed phases is non-linear. The derived time lag is expressed in terms of system parameters and operating conditions in the form of a quadrature. The feature of this solution is that the relative contribution of the pore and surface diffusions is a strong function of upstream pressure when the time lag experiment is operated over the *non-linear* range of the adsorption isotherm. It is this nice feature that we take advantage of to determine the pore and surface diffusivities without resorting to isolation of the pore diffusion by using non-adsorbing gas as a reference, as usually done in many other work. This advantage is not manifested in linear systems where the relative contribution of the pore and surface diffusions is a constant, rendering the delineation of these two processes impossible. Effects of various parameters on the utility of this time lag method are discussed in this paper, and application of the method is demonstrated with experimental data of sulfur dioxide adsorption onto Carbolac carbon (*Proc. Roy. Soc.*, **A271**, 1–18, 1963).

Keywords: time lag, dual diffusion, non-linear adsorption

1. Introduction

Adsorption kinetics in porous media and membrane is generally controlled by the ability of molecules to move from the surrounding bulk fluid into the interior of the medium. More often than not, this transport is governed by diffusion process, and in some cases this is dictated by the entry through some constriction at the mouth of pores or channels where the adsorbed molecules are accommodated. For solids such as activated carbon and silica gel, the transport of molecules are governed by two parallel processes, namely pore diffusion of molecules that are not subject to any potential field, and surface diffusion of adsorbed molecules (Carman and Raal, 1951; Flood et al., 1952; Ross and Good, 1956; Weaver and Metzner, 1966; Gilliland et al., 1958, 1974; Hwang and Kammermeyer, 1966; Sladek et al., 1974; Hwang, 1976; Okazaki et al., 1981; Tamon et al., 1981a, b; Tsujikawa et al., 1987; Kapoor et al., 1989; Do, 1998). The latter motion is constrained by the adsorption potential field between the surface atoms and the adsorbed molecules. The relative contribution of these two processes varies from system to system, and in some systems the surface transport can be very significant and even dominates the total flux. It is important for the purpose of design an adsorption process to know about the characteristics of these two diffusion processes. These characteristics are described by two parameters, known as the pore and surface diffusivities. Pore diffusivity is fairly independent of concentration. Unfortunately the same can not be said about the surface diffusion, as there are ample evidence that the surface diffusivity is a strong function of adsorbed concentration. This concentration dependence is complex, and must be determined experimentally because of our lack of understanding of the solid structure (physical

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as well as chemical) and the nature of interaction between the surface and the adsorbed molecules in terms of molecule mobility. Various experimental methods have been used and many analyses have been proposed to derive the diffusion information. Do and Rice (1991) studied the transient uptake into a single particle, and used the approximate analytical solution for the half time derived by Do (1990) to determine the pore and surface diffusivities from a simple linear plot.

Among the many methods to study the diffusion and adsorption in a porous medium, the time lag method first proposed by Daynes (1920) provides a useful tool to investigate the diffusion of pure gases or vapours through a porous particle. This methods have been utilised by many investigators, notably the series of work by Barrer and his co-workers (Barrer, 1953; Ash et al., 1963). Other workers have also contributed to the better understanding of this method (Frisch, 1957; Kraus and Ross, 1953; van Amerongen, 1964). In this paper, we propose the application of the time lag method to achieve the same objective. Basically, the traditional time lag experiment is carried out, with a particle or many particles mounted by parallel between two chambers. One chamber, initially isolated from the particle and the other chamber, is filled with adsorbate molecules and its volume is large enough so that its pressure is maintained constant during the course of experiment. The other chamber and the particles are initially evacuated, and at time $t = 0+$, the chamber with adsorbate is open and the diffusion of adsorbate molecules through the particle is started. Because of the accumulation of molecules in the particle, both in free and adsorbed forms, the pressure of the downstream chamber remains zero for some time. It is only when the most of the adsorbed sites within the particle are equilibrated the pressure of the receiving chamber starts to rise and as time progresses this pressure versus time will reach a linear asymptote. This linear asymptote will intersect the time axis at a time called the time lag because this time represents the lag time required for the molecule to spend its life within the particle. This time lag is a function of system parameters as well as the operating conditions. Of particular importance to us is its dependence on the pore and surface diffusivities. We will show in this paper that such dependence can be taken advantage of to determine these diffusivities, and this is only achievable when we operate the system in the non-linear range of the adsorption isotherm. In the linear range, however, only the combination of pore and surface diffusivities is derived, and therefore unless one is known a-priori the values of pore and surface diffusivities can not be derived.

2. Time Lag in Porous Media with Adsorption

To analyse the problem of time lag, we assume the mechanism for mass transport within the particle. Pore and surface diffusions are assumed to occur in parallel, and at any local point within the particle the equilibrium is assumed to establish between the two phases. Isothermal conditions are also assumed.

The adsorbate molecules inside the particle are either in the free form (that is no influence of the adsorption field) or in the adsorbed form. The fraction of the particle volume that the adsorbate molecules would occupy as free form is denoted as ε. This means that if C is the concentration of the free molecules, then the number of molecules in the free form within the particle is εC. For the adsorbed molecules, we could define their concentration as moles per unit mass of the particle. Here we define this adsorbed concentration as mole per unit volume of the particle minus the volume that would be occupied by the free molecule. If we denote this concentration as C_μ, then the number of moles of adsorbate per unit particle volume in the adsorbed form is $(1-\varepsilon)C_\mu$. Thus the total number of mole per unit particle volume is

$$\varepsilon C + (1-\varepsilon)C_\mu \tag{1}$$

If the adsorbed concentration is taken as mole per unit mass q, then its relationship with C_μ is simply $\rho_p q = (1-\varepsilon)C_\mu$, where ρ_p is the particle density. Assuming an ideal gas law behaviour, the concentration C is related to the pressure as $C = P/RT$.

The diffusion fluxes of the free molecules and the adsorbed molecules are assumed to take the Fickian law (moles per unit total cross-sectional area per time):

$$J = -\varepsilon D_p \frac{\partial C}{\partial x} \tag{2a}$$

$$J_\mu = -(1-\varepsilon) D_\mu \frac{\partial C_\mu}{\partial x} \tag{2b}$$

The pore diffusivity is usually independent of concentration (unless the viscous flow becomes important compared to the Knudsen flow). When Knudsen diffusion is dominating, the pore diffusivity will take the form:

$$D_{\mathrm{p}} = \frac{1}{\tau^2}\left(\frac{2r}{3}\sqrt{\frac{8RT}{\pi M}}\right) \tag{2c}$$

where r is the average pore radius, and τ^2 is the tortuosity factor, accounting for the pore shape and orientation. For random pore orientation the tortuosity factor is 3 (Johnson and Stewart, 1965). For general solid this parameter is obtained experimentally, and the ratio ε/τ^2 can be treated as the structural parameter of the given solid. The surface diffusivity is assumed to be a function of the adsorbed concentration. We shall take it in a general form, and shall deal with some specific form later to illustrate the utility of the solution.

The equilibrium relationship between the two phases is taken to be:

$$C_\mu = f(C) \tag{3}$$

Having defined the concentrations, the fluxes and the equilibrium relationship between the two phases, we can derive the mass balance equation to describe the concentration distribution within the particle. It takes the following form:

$$\begin{aligned}\varepsilon\frac{\partial C}{\partial t} &+ (1-\varepsilon)\,\frac{\partial C_\mu}{\partial t}\\ &= \frac{\partial}{\partial x}\left[\varepsilon D_{\mathrm{p}}\,\frac{\partial C}{\partial x} + (1-\varepsilon)D_\mu(C_\mu)\,\frac{\partial C_\mu}{\partial x}\right]\end{aligned} \tag{4a}$$

Making use of the local equilibrium relationship between the two phases, we finally derive the following equation written in terms of the concentration of the free species:

$$G(C)\,\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[H(C)\,\frac{\partial C}{\partial x}\right] \tag{4b}$$

where the two functions $G(C)$ and $H(C)$ take the form:

$$G(C) = \varepsilon + (1-\varepsilon)\,f'(C) \tag{4c}$$

$$H(C) = \varepsilon D_{\mathrm{p}} + (1-\varepsilon)D_\mu(f(C))\,f'(C) \tag{4d}$$

For the time lag experiments we have described in the introduction, the initial and boundary conditions will take the following mathematical form:

$$t = 0; \quad C = 0 \tag{4e}$$

$$x = 0; \quad C = C_0 \tag{4f}$$

$$x = L; \quad C \approx 0 \tag{4g}$$

where C_0 is the adsorbate concentration of the supply chamber, which remains constant during the whole course of experiment. The boundary condition at the exit of the particle can be maintained such that the concentration at the exit face of the particle is always much lower than the supply concentration. This is achieved very easily experimentally.

The brute force approach of solving the above mass balance equation is only by numerical means. Such an approach loses the utility of deriving analytical picture about the system behaviour. If the time lag information is what we want, then the approach of Frisch (1957) is the most useful as it will provide the means to obtain the time lag without solving the transient distribution of concentration within the particle. The solution methodology of this approach is given in the Appendix 1. The solution for the time lag for this mass balance equation is:

$$t_{\mathrm{lag}} = \frac{L^2\int_0^{C_0} G^*(u)H(u)\left(\int_u^{C_0} H(w)\,dw\right)du}{\left(\int_0^{C_0} H(u)\,du\right)^3} \tag{5a}$$

where the function $G^*(u)$ is given by

$$G^*(u) = \int_0^u G(w)\,dw = \varepsilon u + (1-\varepsilon)\,f(u) \tag{5b}$$

As seen in the time lag solution, we see that the time lag is a function of the equilibrium parameters, which are embedded in the function G, the pore and surface diffusivities, which are embedded in the function H, the length of the particle L, and the upstream concentration C_0. This dependence can be investigated by simply evaluating the quadrature numerically for any arbitrary functional form for H and G. To illustrate the methodology, we will investigate the following situations:

1. Linear adsorption isotherm and constant surface diffusivity
2. Langmuir isotherm and Darken form surface diffusivity
3. Arbitrary adsorption isotherm and the product $D_\mu f'(C)$ (which is known in the literature as the permeability) takes the following polynomial form

$$D_\mu\,f'(C) = \sum_{j=0}^{N}\alpha_j C^j$$

The last case is a general case and it is applicable to many systems where the surface diffusivity does not follow the Darken relation. We shall illustrate this method with the experimental data of sulfur dioxide adsorption on Carbolac carbon (Ash et al., 1963).

Case 1. Linear isotherm and constant surface diffusivity: First we consider the simplest case where the adsorption isotherm is linear

$$C_\mu = KC \tag{6}$$

where K is the Henry constant. The linear isotherm is applicable when the system pressure is very low. Under this condition, the loading on the surface is also very low, and this usually results in a constant surface diffusivity, denoted as the surface diffusivity at zero loading D_μ^0. Here the upper-script "0" denotes zero loading. With this linear isotherm, the functions $G(C)$ and $H(C)$ are *independent* of concentration as given below:

$$G(C) = \varepsilon + (1-\varepsilon)K \tag{7a}$$

$$H(C) = \varepsilon D_\mathrm{p} + (1-\varepsilon)KD_\mu^0 \tag{7b}$$

Substitution of Eqs. (7) into Eq. (5a) gives the following solution for the time lag under the linear isotherm condition.

$$t_\mathrm{lag} = \frac{L^2[\varepsilon + (1-\varepsilon)K]}{6\left[\varepsilon D_\mathrm{p} + (1-\varepsilon)D_\mu^0 K\right]} \tag{8a}$$

or multiplying it by AC_0, where A is the cross-sectional area of the particle, we have:

$$t_\mathrm{lag} = \frac{1}{6}\frac{AL[\varepsilon C_0 + (1-\varepsilon)C_{\mu 0}]}{A\left[\varepsilon D_\mathrm{p} C_0 + (1-\varepsilon)D_\mu^0 C_{\mu 0}\right]/L} \tag{8b}$$

Observing the Eq. (8b), we note that the time lag is basically the ratio of

(a) the capacity of the particle in equilibrium with the linear concentration profile $C_0(1 - x/L)$:

$$\left(\frac{1}{2}\right)AL[\varepsilon C_0 + (1-\varepsilon)C_{\mu 0}], \tag{9a}$$

(b) to the mass transfer rate across the particle,

$$A\left[\varepsilon D_\mathrm{p} C_0 + (1-\varepsilon)D_\mu^0 C_{\mu 0}\right]/L \tag{9b}$$

This observation means that the time lag is simply one third of the time required to equilibrate the particle with adsorbate having a linear concentration profile across the particle when the rate of mass transfer is maintained at the steady state rate as given in Eq. (9b).

The independence of the time lag with the upstream pressure means that we *can not* learn any extra information from the variation of the upstream concentration. What this means is that if the time lag is measured over the linear range of the adsorption isotherm, the combined diffusivity of pore and surface diffusion $[\varepsilon D_\mathrm{p} + (1-\varepsilon)D_\mu^0 K]$ will be obtained. The relative contribution of pore and surface diffusions to the total flux is not known unless we know either the pore diffusivity or the surface diffusivity a-priori (usually pore diffusivity). Traditionally, this is achieved by carrying out an experiment with *non-adsorbing gas*, such as helium. We must be careful that in some solids such as very fine pore active carbon, helium may adsorb (absorb) to some degree even at room temperature. However, if it is taken to be non-adsorbing, in principle either the time lag for non-adsorbing gas (obtained by setting $K = 0$ in Eq. (8a))

$$t_\mathrm{lag} = \frac{L^2}{6D_\mathrm{p}} \tag{10}$$

or the steady state flux through the particle

$$\frac{\varepsilon D_\mathrm{p} C_0}{L} \tag{11}$$

could be used to determine the pore diffusivity. Since the particle used in the time lag experiment is typically of the order of 1 cm, the time lag for non-adsorbing gas is too short to practically measure, the steady state flux is therefore used to determine the pore diffusivity. The following example shows the time lag and the pressure rise versus time for the case of non-adsorbing helium diffusing through a typical carbon particle.

Particle length	0.5 cm
Particle porosity	0.33
Particle cross sectional area	0.03 cm^2
Mean pore radius	0.1 micron
Tortuosity factor	3
Temperature	298 K
Molecular weight	4
Volume of the receiving reservoir	20 cc
Upstream concentration	5×10^{-6} mole/cc

With the above values, the Knudsen diffusivity is calculated as 0.28 cm^2/sec. Using Eqs. (10) and (11) the time lag for helium is 0.15 sec and the flux is 9.24×10^{-7} mole/cm^2/sec. With this flux, the pressure rise versus time in the receiving reservoir is calculated to be 0.026 Torr/sec. The time lag for a non-adsorbing gas is too short to measure unless the particle is very long. Therefore the flux (or the pressure rise versus time) is used to calculate the pore diffusivity of the non-adsorbing gas.

Once the helium pore diffusivity is obtained, the pore diffusivity of any adsorbate is calculated assuming the square root dependence holds, that is:

$$D_{\mathrm{p}} = D_{\mathrm{p,He}}\sqrt{\frac{M_{\mathrm{He}}}{M}} \tag{12}$$

Equation (12) is generally valid as long as the pore network for pore diffusion for helium is the same as that for the adsorbate concerned. This is the implicit assumption that many work in the literature have assumed in calculating the adsorbate pore diffusivity. Once the pore diffusivity is calculated, the surface diffusivity can be obtained by subtracting the pore diffusivity from the combined diffusivity, $[\varepsilon D_{\mathrm{p}} + (1-\varepsilon)D_\mu^0 K]$. This is the usual approach adopted by many researchers in the literature.

The approach we propose here takes the advantage that the contributions of the pore and surface diffusion vary with the upstream concentration. This utility can provide us a means to extract the pore and surface diffusivities without resorting to the helium experiment, which implicitly assumes that helium is non-adsorbing and the helium flow path is the same as that of the adsorbate. We shall show below the case where the adsorption isotherm follows a Langmuir equation.

Case 2: Langmuir isotherm and Darken form surface diffusivity: The equilibrium relationship is described by the Langmuir equation

$$C_\mu = C_{\mu\mathrm{s}}\frac{bC}{1+bC} \tag{13}$$

We will assume here the surface diffusivity to follow the Darken relationship (Darken, 1948; Higashi et al., 1963; Yang et al., 1973)

$$D_\mu = D_\mu^0 \frac{\partial \ln C}{\partial \ln C_\mu} \tag{14a}$$

With the isotherm taking the Langmuir equation the surface diffusivity will take the following explicit form in terms of the adsorbed concentration

$$D_\mu = \frac{D_\mu^0}{1 - C_\mu / C_{\mu\mathrm{s}}} \tag{14b}$$

For this case, the functions $G(C)$ and $H(C)$ become:

$$\begin{aligned} G(C) &= \varepsilon + \frac{(1-\varepsilon)K}{(1+bC)^2}; \\ H(C) &= \varepsilon D_{\mathrm{p}} + \frac{(1-\varepsilon)KD_\mu^0}{(1+bC)} \end{aligned} \tag{15}$$

where $K = bC_{\mu\mathrm{s}}$. Substitution of the above expressions for $G(C)$ and $H(C)$ into the expression for the time lag (Eq. (5)) yields the following solution:

$$t_{\mathrm{lag}} = \frac{L^2}{D_{\mathrm{p}}} \frac{\int_0^1 y\left[1 + \frac{(1-\varepsilon)K}{\varepsilon(1+\lambda y)}\right]\left[1 + \frac{\delta}{(1+\lambda y)}\right]\left[(1-y) + \frac{\delta}{\lambda}\ln\left(\frac{1+\lambda}{1+\lambda y}\right)\right] dy}{\left[1 + \frac{\delta}{\lambda}\ln(1+\lambda)\right]^3} \tag{16a}$$

where the parameter δ is a measure of the relative importance of the surface diffusion to the pore diffusion

$$\delta = \frac{(1-\varepsilon)KD_\mu^0}{\varepsilon D_{\mathrm{p}}}; \qquad \lambda = bC_0 \tag{16b}$$

The parameter λ is a measure of the isotherm nonlinearity. The isotherm is called linear when this parameter is much less than unity, and is strongly non-linear when it is greater than about 10; otherwise it is called moderately non-linear. When the upstream concentration is small (that is in the linear range of the isotherm), the time lag of Eq. (16a) reduces to Eq. (8a), derived earlier for the case of linear isotherm and it is independent of upstream concentration.

Equation (16) can be easily evaluated by numerically studying the dependence of the time lag on the upstream concentration. Figure 1 shows the plot of the time lag

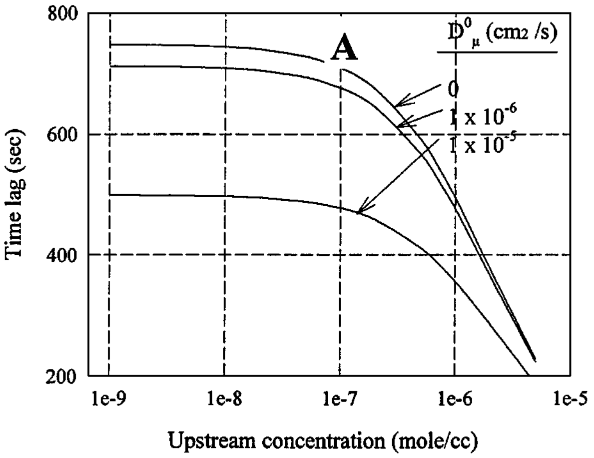


Figure 1. Typical plot of time lag versus the upstream concentration with surface diffusivity as the varying parameter.

versus C_0 for a typical case of diffusion of propane through a pellet of activated carbon. The surface diffusivity is the varying parameter in the figure. The values of the parameters used in the generation of Fig. 1 are: saturation capacity, $C_{\mu s} = 5.6 \times 10^{-3}$ mole/g, adsorption affinity, $b = 1.1 \times 10^6$ cc/mole, particle length, $L = 0.5$ cm, pore size, $r = 0.8\,\mu$, tortuosity factor, $\tau^2 = 4.9$, particle porosity, $\varepsilon = 0.33$, temperature, $T = 283$ K.

We see that the time lag is very sensitive to the upstream concentration over the region where the adsorption isotherm is non-linear.

The curve corresponding to the case of $D_\mu = 0$ (that is no surface diffusion) has the following analytical solution (by setting δ to zero in Eq. (16a) and carrying the integration):

$$t_{\text{lag}} = \frac{L^2}{6(\varepsilon D_{\text{p}})}[\varepsilon + (1-\varepsilon)K \cdot F(\lambda)] \tag{17}$$

where $F(\lambda)$ is a function of the isotherm nonlinearity (hereafter called the isotherm nonlinearity factor) and is given by:

$$F(\lambda) = \frac{6}{\lambda}\left\{\frac{1}{2} + \frac{1}{\lambda^2}[\lambda - (1+\lambda)\ln(1+\lambda)]\right\}; \tag{18}$$

The curve A, corresponding to no surface diffusion, in Fig. 1 is the upper limit for the family of curves shown in the figure. The surface diffusion reduces the time lag as expected.

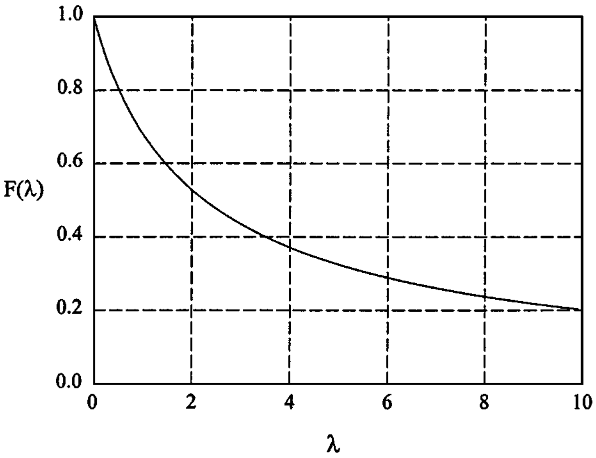


Figure 2. Plot showing the effect of nonlinearity on the time lag.

In the limit of linear isotherm (low concentration) the time lag given in Eq. (17) is reduced to:

$$\lim_{\lambda\to 0} t_{\text{lag}} = \frac{L^2[\varepsilon + (1-\varepsilon)K]}{6(\varepsilon D_{\text{p}})} \tag{19}$$

The effect of the isotherm nonlinearity can now be seen by studying the reduced time lag scaled against the time lag corresponding to zero loading:

$$R = \frac{t_{\text{lag}}}{\lim_{\lambda\to 0} t_{\text{lag}}} = \frac{[\varepsilon + (1-\varepsilon)K \cdot F(\lambda)]}{\varepsilon + (1-\varepsilon)K} \approx F(\lambda) \tag{20}$$

The approximation of the above equation is justified for most adsorption systems where the capacity of the adsorbed phase is much larger than that of the fluid phase. Figure 2 shows the variation of the function $F(\lambda)$ versus λ.

As seen in the figure the isotherm nonlinearity of a convex isotherm reduces the time lag. This is expected as a double in the concentration in the fluid phase corresponds to *less than double* in the adsorbed phase concentration due to the convexity of the isotherm, and hence the driving force for permeating through the medium is enhanced, resulting in a lower time lag.

We have seen that the isotherm nonlinearity of a convex isotherm causes a reduction in the time lag. However, this is not the only reason. Other factors such as the viscous flow, the surface diffusion also contribute to the reduction. It is important for us to delineate these contributions. The viscous effect can either be determined from steady state flow experiment with non-adsorbing gas over a range of pressure. Since the viscous flow is pressure dependent while the Knudsen flow is not, the delineation between the two is always possible (Do, 1998). To delineate the pore and surface diffusion is always an interesting task, and this is one of the objectives of this paper.

Let us return to the case of no surface diffusion and investigate the situation where the adsorption isotherm is strongly non-linear (that is $\lambda \gg 1$). For this case, we have:

$$\lim_{\lambda\to\infty} t_{\text{lag}} = \frac{L^2}{6(\varepsilon D_{\text{p}})}\left[\varepsilon + (1-\varepsilon)\frac{3C_{\mu\text{s}}}{C_0}\right] \tag{21}$$

The second term in the RHS of the above equation is generally larger than the first term, so the time lag equation for the case of irreversible isotherm is reduced to:

$$\lim_{\lambda\to\infty} t_{\text{lag}} \approx \frac{L^2}{6(\varepsilon D_{\text{p}})}(1-\varepsilon)\frac{3C_{\mu\text{s}}}{C_0} \tag{22}$$

Thus, we see that the time lag in this case is inversely proportional to the supply reservoir concentration over the range where the isotherm is flat.

Case 3: *Arbitrary isotherm and assumed functional form for surface diffusivity*: The last two cases deal with a case of linear isotherm and a case of Langmuir isotherm. In many systems where the dependence of the surface diffusivity on loading does not follow the Darken relation, we shall assume that the product $D_\mu f'(C)$ takes the following dependence

$$D_\mu f'(C) = \sum_{j=0}^{N} \alpha_j C^j \tag{23}$$

With this dependence, the time lag will take the following quadrature form:

$$t_{\text{lag}} = \frac{L^2}{D_{\text{p}}}\frac{\int_0^1 \left[y + \frac{(1-\varepsilon)}{\varepsilon}\frac{f(C_0 y)}{C_0}\right]\left[1 + \frac{(1-\varepsilon)}{\varepsilon}\sum_{j=0}^{N}\beta_j y^j\right]\left[(1-y) + \frac{(1-\varepsilon)}{\varepsilon}\sum_{j=0}^{N}\frac{\beta_j}{j+1}(1-y^{j+1})\right]dy}{\left[1 + \frac{(1-\varepsilon)}{\varepsilon}\sum_{j=0}^{N}\frac{\beta_j}{j+1}\right]^3} \tag{24a}$$

where

$$\beta_j = \frac{\alpha_j C_0^j}{D_{\text{p}}} \tag{24b}$$

Thus for any arbitrary isotherm the time lag can be evaluated from the above quadrature. When the experimental time lag versus the upstream concentration is available, the above equation can be used in an optimisation routine to extract the pore diffusivity and the constants α_j. Knowing these constants the functional dependence of the surface diffusivity versus concentration loading can be obtained as:

$$D_\mu = \frac{\sum_{j=0}^{N}\alpha_j C^j}{f'(C)} \tag{25}$$

With this approach, we can avoid the need of invoking the Darken relationship which may not be satisfied in many practical systems.

3. Discussion

3.1. Simulations

We have seen that the time lag is a useful means to determine the kinetics parameters, such as pore and surface diffusivities. It is simple in the sense that the only thing that experimentalists need to measure is the time at which the linear asymptote of the downstream pressure versus time intersects the time axis, called the time lag. If the adsorption isotherm is linear, the time lag can be used to determine the combined diffusivity, and the pore and surface diffusivities can not be delineated separately. To do this, the diffusion of non-adsorbing gas must be used to isolate the contribution of the pore diffusion as we have discussed in the last section. We argue here that this delineation is possible if we conduct the experiment in the nonlinear range, over which the relative contribution of the pore and surface diffusion is a function of upstream concentration. The reason why this is possible is because when the upstream concentration is doubled, the pore diffusion flux is also doubled, assuming the pore diffusivity is constant. Let us assume now that the isotherm is convex (that is favourable isotherm) then a double increase in the upstream concentration is resulted in a less than double adsorptive capacity. This less than double adsorptive capacity coupled with an increase in the surface diffusivity will result in a reduction in the time lag. Hence the time lag versus upstream concentration is a decreasing function as we have shown in Fig. 1. This information can be used to our advantage to determine the pore and surface diffusivities as we shall show later in the analysis of experimental data section. But first we would like to explore how the time lag for the case of nonlinear isotherm would behave when the key parameters of the system are varied. The parameters that we would like to investigate are

(i) particle length
(ii) adsorption affinity

We shall take the case of Langmuir isotherm and Darken form surface diffusivity to illustrate the effects of the above parameters. Other forms of adsorption isotherm and surface diffusivity yield similar conclusions. Readers interested in other isotherms and other forms of surface diffusivity can substitute their relevant equations into Eq. (5) to derive the corresponding time lag.

Effect of particle length: The time lag equation for the case of Langmuir isotherm and Darken form surface diffusivity is given in Eq. (16), where we see that the time lag is proportional to the square of the particle length. Particle length is easily varied experimentally, and therefore it can be used to check the validity of the diffusive type processes. Note that while the time lag is proportional to the square of the particle length, the steady state mass transfer rate per unit particle cross-section area is:

$$J_{\mathrm{SS}} = \frac{1}{L}\left[\varepsilon D_{\mathrm{p}} C_0 + \frac{(1-\varepsilon)KD_{\mu}^{0}}{b}\ln(1+bC_0)\right] \quad (26)$$

which is inversely proportional to the particle length.

Effect of affinity: When adsorbates of different strength of adsorption are used in experiments, we need to know how this would affect the time lag as well as steady flux. The dependence on the affinity is not as clear as that for particle length. So we shall investigate this numerically. We know that when the adsorption affinity is varied because of the use of different adsorbates, the pore and surface diffusivities are *also* varied. Usually for a given family of adsorbates, say hydrocarbon paraffins, the adsorption affinity increases with the carbon number while the pore and surface diffusivities decrease with the carbon number. To get a realistic physical picture, we use the experimental data of ethane and propane on a commercial activated carbon obtained in our laboratory. The equilibrium and kinetic parameters for these two adsorbates are given in the following table.

	Ethane	Propane
Temperature, K	283	283
Saturation capacity, mole/cc	6×10^{-3}	5.6×10^{-3}
Adsorption affinity, cc/mole	1.2×10^{5}	1.1×10^{6}
Molecular weight, g/mole	30	44
Surface diffusivity, cm^2/s	3.5×10^{-5}	9×10^{-6}

The properties of the activated carbon particle and the receiving reservoir volume are given below.

Particle length	0.5 cm
Particle porosity	0.33
Particle cross sectional area	0.03 cm^2
Mean pore radius	0.8 micron
Tortuosity factor	4.9
Volume of the receiving reservoir	20 cc

Figure 3 shows the time lag of weaker adsorbate (ethane) and stronger adsorbate (propane) versus the upstream concentration. The adsorption affinity of propane is about 10 times larger than that of ethane, but the time lag of propane is only about 7 times of

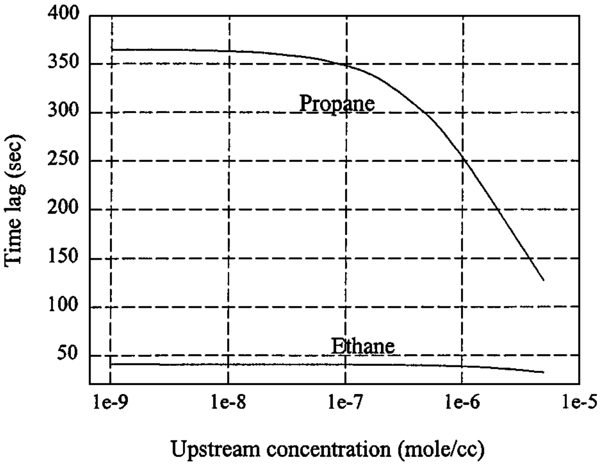


Figure 3. Effect of the adsorbate affinity on the time lag versus concentration.

that of ethane over the linear range of the isotherm ($C_0 < 1 \times 10^{-8}$ mole/cc). This is an indication of the presence of the surface diffusion because as seen in Eq. (8a) for the case of linear isotherm, if the surface diffusion is absent the time lag is somewhat proportional to the adsorption affinity. Therefore the surface diffusion is important for ethane and propane.

3.2. *Parameter Determination*

We have shown from the simulation that when the time lag experiment is operated over the nonlinear range of the adsorption isotherm, the delineation of the pore and surface diffusion is possible because the relative contribution between the pore diffusion and the surface diffusion varies with the upstream concentration. What this means is that if the time lags are measured at various upstream concentrations the pore and surface diffusivities can be extracted simultaneously without the need of calculating or estimating the pore diffusivity. This direct determination of the pore and surface diffusivities eliminates the possibility of incorrect calculation of the pore diffusivity. We shall illustrate the simultaneous determination of pore and surface diffusivities using the following information on the particle and the adsorption isotherm

Particle length (cm)	0.3
Particle porosity (−)	0.33
Adsorption affinity (cc/mole)	1.1×10^7
Saturation capacity (mole/cc)	5.6×10^{-3}

The measured time lags for various upstream concentrations are given below.

C_0 (mole/cc)	5×10^{-8}	7×10^{-8}	1×10^{-7}	2×10^{-7}
Time lag (sec)	2914	2728	2495	1970

We carry out the optimisation with MATLAB (using the FMINS program) on Eq. (16) and extract the pore and surface diffusivities as 0.399 and 1×10^{-6} cm^2/s. The convergence is always reached no matter what the initial guess is. This is simply due to the different relative contribution between the pore and surface diffusion over the nonlinear range of the isotherm. Such a delineation is not possible if we conduct the experiment over the linear range of the isotherm, where the relative contribution between the two diffusion mechanisms is always a constant (see Eq. (8)).

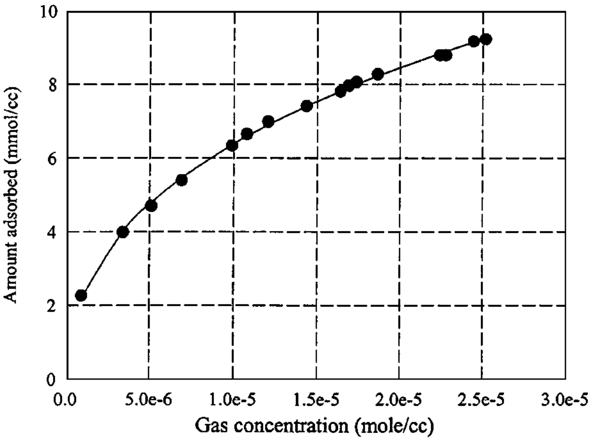


Figure 4. Adsorption isotherm of sulfur dioxide on Carbolac carbon at 0°C (Data of Ash et al., 1963).

We further illustrate the method with the experimental data of sulfur dioxide on Carbolac I carbon obtained by Ash et al. (1963). The isotherm of sulfur dioxide at 0°C can be described well by a Toth adsorption isotherm equation as shown in Fig. 4. The equilibrium parameters of the Toth equation

$$C_\mu = C_{\mu s} \frac{bC}{[1 + (bC)^t]^{1/t}}$$

are $b = 1.533 \times 10^6$ cc/mole, $t = 0.125$ and $C_{\mu s} = 0.468$ mol/cc.

The vapour pressure of sulfur dioxide at 0°C is 1156 Torr (Perry, 1973). The particle used by Ash et al. (1963) has a length of 0.91 cm and a porosity of 0.5. Microscopic examination of the particle has shown that the carbon is composed of microparticle with an average diameter of 100 A. Assuming the average pore size for through pores is about the same order of 100 A, the Knudsen diffusivity calculated for sulfur dioxide at 0°C is 0.02 cm^2/s.

We use Eq. (24) to match with the time lag experimental data (shown as filled circle symbols in Fig. 5). In this equation, we use four constants $\alpha_j (j = 0$ to 3), and carry out the optimisation by minimising the residual between the experimental time lag and the time lag calculated from Eq. (24). The procedure is done with MATLAB optimisation routine (FMINS), and the optimal parameters are found to be:

$$D_p = 0.00838\,\mathrm{cm^2/sec}$$

$$\alpha_0 = 0.04235\,\mathrm{cm^2/sec}$$

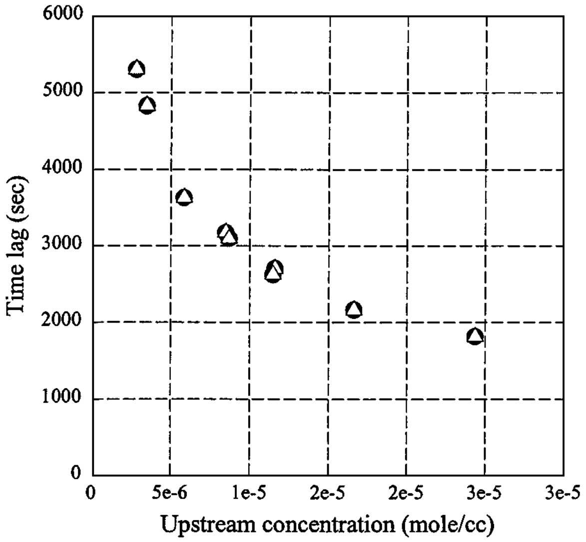


Figure 5. Time lag versus the upstream concentration (calculated from Eq. (24): triangle symbol; exp. data: circle).

$$\alpha_1 = -4.096 \times 10^3 \ (\mathrm{cm^2/sec})/(\mathrm{mole/cm^3})$$

$$\alpha_2 = 1.196 \times 10^8 \ (\mathrm{cm^2/sec})/(\mathrm{mole/cm^3})^2$$

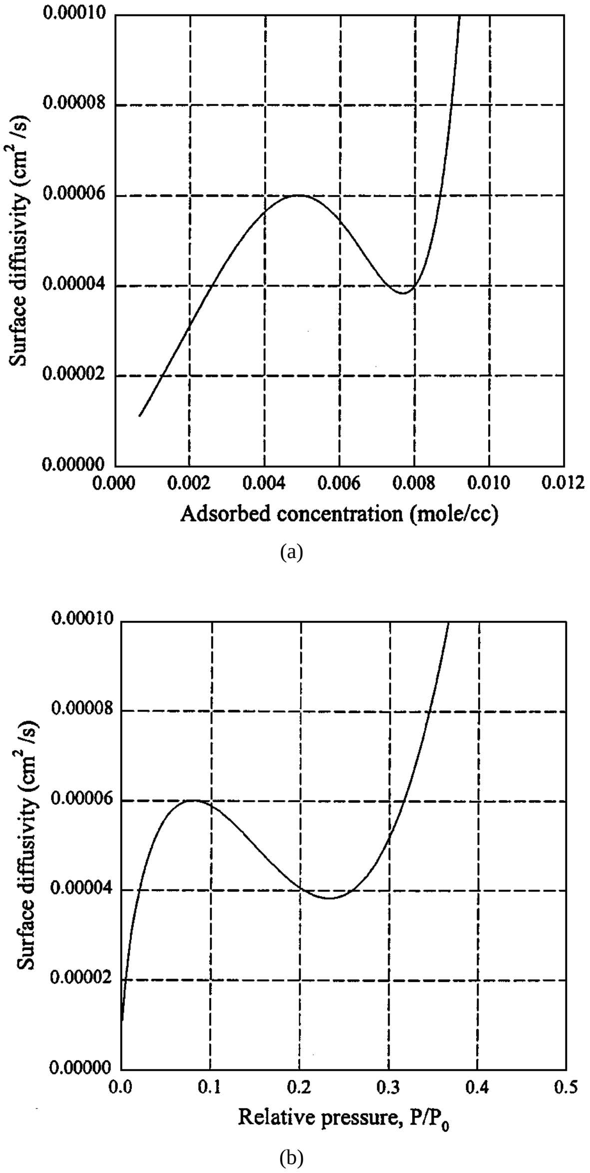
$$\alpha_3 = 1.52 \times 10^7 \ (\mathrm{cm^2/sec})/(\mathrm{mole/cm^3})^3$$

With the extracted pore diffusivity of 0.00838 $\mathrm{cm^2/s}$, the tortuosity factor can be calculated as:

$$\tau^2 = \frac{D_K}{D_p} = \frac{0.02}{0.00838} = 2.4$$

This value of tortuosity is within the range commonly observed for many practical porous solid media (2 to 6).

The time lags calculated from the extracted constants α's are shown in Fig. 5 as triangle symbols, and their agreement with the experimental time lags is very good. With the extracted constants α's, the surface diffusivity is then plotted versus the adsorbed concentration as shown in Fig. 6(a), and versus the relative pressure as shown in Fig. 6(b). We see that the surface diffusivity reaches a maximum, decreases to a minimum, then finally increases with a further increase in the loading. This behaviour is commonly observed for systems with multilayer adsorption (Ash et al., 1963; Kapoor et al., 1989; Haynes and Miller, 1982; Rajniak and Yang, 1996). When the loading is less than the monolayer coverage the surface flow is that of diffusive nature while for loading higher than the monolayer coverage the flow is of hydrodynamic nature. The surface diffusivity at zero loading is calculated as 6×10^{-8} $\mathrm{cm^2/s}$. Although the surface diffusivity at zero loading is of the order of 10^{-7} $\mathrm{cm^2/s}$, the surface diffusivity over the range of loading carried out in the experiment is of the order between 10^{-5} and 10^{-4} $\mathrm{cm^2/s}$.



(a)

(b)

Figure 6. (a) Calculated surface diffusivity versus the adsorbed concentration for sulfur adsorption on Carbolac. (b) Calculated surface diffusivity versus the relative pressure for sulfur adsorption on Carbolac.

To evaluate the relative contribution of the pore and surface diffusion, we evaluate the ratio of the surface diffusion flux to the pore diffusion flux and present

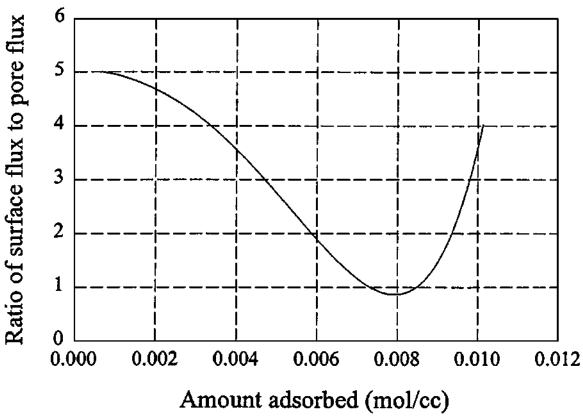


Figure 7. Plot of the ratio of the surface diffusion flux to the pore diffusion flux for sulfur dioxide in Carbolac.

the result graphically on Fig. 7 as a function of the amount adsorbed. Here we see that when the loading is low the surface diffusion dominates and its flux contributes more than 80% of the total flux. When the loading approaches the monolayer coverage (about 0.006 mole/cc), both pore and surface diffusion equally contribute to the total flux. Finally when the loading is beyond the monolayer coverage the surface diffusion again dominates and this is usually attributable to the hydrodynamic nature of the adsorbed molecules.

Conclusion

We have presented in this paper an analysis of time lag for systems where the mass transfer is controlled by a dual diffusion mechanism (pore and surface diffusion). Here we take advantage of the fact that the relative contribution of the pore and surface diffusions varies over the *nonlinear* range of the isotherm to determine their diffusivities without the a-priori estimation of the pore diffusivity as done by past work in the literature. Such pore diffusivity, if incorrectly estimated, can cause an erroneous determination of the surface diffusivity. Our method completely eliminates this, and it allows the users to determine the two diffusivities simultaneously. We have demonstrated this with experimental data of sulfur dioxide on Carbolac carbon.

Appendix 1: Frisch Method for Solving Eq. (4)

To obtain the time lag using the Frisch's method, the steady state concentration distribution must be determined. By setting the time derivative of Eq. (4a) to zero, and we get:

$$\frac{d}{dx}\left[H(C_\infty)\,\frac{dC_\infty}{dx}\right] = 0 \qquad \text{(A1)}$$

The capacity function $G(C)$ is not seen in the steady state equation. This is simply due to the capacity does not affect the distribution at steady state, which is only affected by how fast molecules are transported through the particle.

Solution of Eq. (A1) subject to the constant boundary conditions (4f, g) is written in the following implicit form:

$$\int_{C_\infty(x)}^{C_0} H(u)\,du = \frac{x}{L}\left(\int_0^{C_0} H(u)\,du\right) \qquad \text{(A2)}$$

Knowing this concentration of the free species as function of distance, the concentration of the adsorbed phase at steady state is simply given by:

$$C_{\mu\infty} = f(C_\infty(x)) \qquad \text{(A3)}$$

To obtain the time lag expression, we integrate Eq. (4a) with respect to x from L to x and obtain:

$$\int_L^x G(C)\,\frac{\partial C}{\partial t}\,dz = H(C)\,\frac{\partial C}{\partial x} - H(C)\,\frac{\partial C}{\partial x}\bigg|_L \qquad \text{(A4)}$$

The second term in the RHS of the above equation is the flux entering the receiving chamber, which is only a function of time. We shall denote it $J_L(t)$. Integrating the above equation again with respect to x from 0 to L, we get:

$$\int_0^L \int_L^x G(C)\,\frac{\partial C}{\partial t}\,dz\,dx = \int_{C_0}^0 H(u)\,du + [J_L(t)]L \qquad \text{(A5)}$$

Finally we integrate this result with respect to time from $t = 0$ to t to obtain the following result for the amount collected by the receiving chamber per unit area of the medium:

$$\frac{Q_L(t)}{A} = \int_0^t J_L(t)\,dt$$
$$= \left[\frac{1}{L}\int_0^{C_0} H(u)\,du\right]t - \frac{1}{L}\int_0^L \int_L^x G^*(C)\,dz\,dx \qquad \text{(A6a)}$$

where $G^*(C)$ is given by:

$$G^*(C) = \int_0^C G(u)\,du \tag{A6b}$$

When time is sufficiently large, the above equation will take the form, written so that the intercept with the time axis can be seen:

$$\lim_{t\to\infty} \frac{Q_L(t)}{A} = \left[\frac{1}{L}\int_0^{C_0} H(u)\,du\right](t - t_{\text{lag}}) \tag{A7a}$$

where the time lag is given by:

$$t_{\text{lag}} = \frac{\int_0^L \int_x^L G^*(C_\infty)\,dz\,dx}{\int_0^{C_0} H(u)\,du} = \frac{\int_0^L xG^*(C_\infty(x))\,dx}{\int_0^{C_0} H(u)\,du} \tag{A7b}$$

Making use of the steady state concentration $C_\infty(x)$ as given in Eq. (A2), we now derive the time lag expression in terms of

(i) particle length
(ii) upstream concentration
(iii) the capacity function $G(C)$, which embeds the equilibrium parameters
(iv) the kinetic function $H(C)$, which embeds the kinetic parameters

$$t_{\text{lag}} = \frac{L^2 \int_0^{C_0} G^*(u)H(u)\left(\int_u^{C_0} H(w)\,dw\right)du}{\left(\int_0^{C_0} H(u)\,du\right)^3} \tag{A8}$$

The explicit expression for this time lag depends on the choice of the adsorption isotherm $f(C)$ and the functional form for $D_\mu(C_\mu)$.

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