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CONTRIBUTION OF CONCENTRATION-DEPENDENT SURFACE DIFFUSION TO RATE OF ADSORPTION

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Abstract—A model is presented which describes the intraparticle mass transfer considering both gas phase and adsorbed-phase diffusion. The model accounts for the concentration dependence of surface diffusion, and uses the Langmuir isotherm to describe the adsorption equilibria. A parametric study is presented showing the effects of various variables on the overall uptake curve and intraparticle concentration profiles. It is shown that surface diffusion contributes significantly to the overall intraparticle mass transfer. More importantly, inclusion of concentration dependence of surface diffusivity in the model influences significantly both the overall uptake and the intraparticle concentration profiles. The overall effect of concentration dependence of surface diffusivity is to enhance the rate of uptake during adsorption, and decrease it during desorption. Also, experimental uptake curves are presented for *n*-hexane on BPL activated carbon at two temperatures, and the data are correlated with the model. The surface diffusivities calculated from the model ignoring the concentration dependence of surface diffusivity are higher by a factor of 2–3 compared to the correct values obtained from the concentration-dependent model.

INTRODUCTION

Intraparticle mass transfer in adsorption systems has been studied extensively both experimentally and theoretically. Theoretical effort has generally included one of the following three models: (1) the pore diffusion model, (2) the "solid diffusion" model, and (3) the pore and surface diffusion model (Do and Rice, 1987; Wakao and Kaguei, 1982). Surface diffusion can contribute significantly to the overall intraparticle mass transfer under certain conditions; thus, in this work we limit the discussion only to the pore and surface diffusion models.

A number of studies describing the overall rate of adsorption in terms of pore and surface diffusion are given in the literature; however, only a few of them are discussed below. Much work has been done on models (Rimpel *et al.*, 1968; Schneider and Smith, 1968; Do, 1983; Ruthven, 1984; Costa *et al.*, 1985; Klotz and Rousseau, 1988; Bhatia, 1988) with constant surface diffusivity and linear adsorption equilibria.

Haynes and Miller (1982), Aris (1983), Do and Rice (1987), Leyva-Ramos and Geankoplis (1985) and Schork and Fair (1988), among others, developed pore and surface diffusion models assuming surface diffusivity to be constant as in studies mentioned earlier, but used nonlinear adsorption equilibria.

Doong and Yang (1986) and Sun and Meunier (1987) considered the concentration-dependent surface diffusion. Sun and Meunier (1987) presented a model based on the gradient of chemical potential as the driving force, and simultaneous pore and surface diffusion to describe sorption in a microporous particle. They used Dubinin's adsorption isotherm. Doong and Yang (1986) employed a pore–surface diffusion model to describe intraparticle mass transfer in their pressure swing adsorption model. They considered a Langmuir isotherm and concentration-dependent surface diffusivity. However, to simplify their analysis, they assumed parabolic concentration profiles in the particle, and derived linear driving force expressions. Also, they applied the concentration dependence to the average surface diffusivity in the paricle based on the average amount adsorbed in the particle.

In this paper, we present a model to describe the uptake rate in a porous particle, considering diffusion in both the gas phase and the adsorbed phase. The surface diffusivity is correctly taken as a function of the local adsorbate concentration, and the adsorption equilibria are described by the Langmuir isotherm. Using this model, the transient overall uptake and the concentration profiles in the particle are calculated for various parametric values. Also, experimental uptake curves are presented for *n*-hexane on BPL activated carbon at two temperatures. By correlating the experimental uptake data, the surface diffusivity values are calculated, and the effect of ignoring the concentration dependence of the surface diffusivity on the value of the determined surface diffusivity is shown.

THEORETICAL MODEL

Consider a spherical particle in an adsorber bed. The mass balance inside the pore of this particle can be written as

$$\frac{\partial C}{\partial t} + \frac{1}{r^2}\frac{\partial(r^2 N_r)}{\partial r} + \gamma\frac{\partial q}{\partial t} = 0 \qquad (1)$$

where C is the gas phase concentration in the intraparticle void, q is the amount adsorbed, $\gamma = a_p/\varepsilon_p$, and N_r is the total flux at a radial position r. The flux,

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N_r, includes both gas phase and adsorbed-phase fluxes, and is given by

$$N_r = -D_g \frac{\partial C}{\partial r} - D_s \gamma \frac{\partial q}{\partial r} \tag{2}$$

where D_g is the pore diffusivity, D_s is the surface diffusivity, and $\partial C/\partial r$ and $\partial q/\partial r$ are the gas phase and adsorbed-phase concentration gradients, respectively, at the radial position r. It is assumed that the values of D_g and D_s include their corresponding tortuosity factors. It is further assumed that the gas phase and adsorbed phase are in equilibrium (Yang, 1967, p. 101), and are related by the Langmuir isotherm:

$$q = \frac{q_m b C}{1 + bC}. \tag{3}$$

The surface diffusivity is known to be a function of the adsorbed-phase concentration; surface diffusivity increases with an increase in adsorbed-phase concentration. Several models have been suggested in the literature to describe surface diffusion. These models have been recently reviewed by Kapoor *et al.* (1989). In this study, we used the HIO model proposed by Higashi *et al.* (1963). The HIO model is based on a random walk of molecules from adsorption site to adsorption site on the solid surface. It assumes that the transit time between sites is negligible compared to the residence time on each site, and the molecule immediately bounces off if it encounters a site already occupied by another molecule. According to the HIO model (Yang *et al.*, 1973)

$$D_s = \frac{D_{so}}{1 - \theta} \tag{4}$$

where θ is the fractional surface coverage ($\theta = q/q_m$), and D_{so} is a constant. The parameter D_{so} corresponds to the value of surface diffusivity in the limit of zero fractional surface coverage.

Combining eqs (1)–(4) we get

$$\beta(q) \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 \alpha(q) \frac{\partial q}{\partial r} \right] \tag{5}$$

where

$$\beta(q) = \frac{q_m}{b(q_m - q)^2} + \frac{a_p}{\varepsilon_p}$$

and

$$\alpha(q) = \frac{D_g q_m}{b(q_m - q^2)} + \frac{D_{so} a_p q_m}{\varepsilon_p (q_m - q)}.$$

Equation (5) is the model equation. However, if the surface diffusivity is assumed to be independent of the adsorbed-phase concentration, $\alpha(q)$ becomes

$$\alpha(q) = \frac{D_g q_m}{b(q_m - q)^2} + \frac{\bar{D}_s a_p}{\varepsilon_p} \tag{6a}$$

where

$$\bar{D}_s = \frac{\int_0^{\theta^*} \frac{D_{so}}{1 - \theta} \, d\theta}{\int_0^{\theta^*} d\theta} \text{ and } \theta^* = q^*/q_m. \tag{6b}$$

$\bar{D}_s$ is the average surface diffusivity used as a constant in previous studies in the literature. Results from eqs (5) and (6) will provide a basis for assessing the effects of the concentration dependence of D_s.

The initial and boundary conditions for the model are given below. It is assumed that, at time $t = 0$, there exists a known concentration in the particle:

$$\begin{aligned} &\text{At } t = 0\text{:} \quad q = q_i \\ &\text{At } t > 0\text{:} \quad \text{at } r = 0,\ \partial q/\partial r = 0 \\ &\qquad\qquad\ \ \text{at } r = R,\ q = q^*. \end{aligned} \tag{7}$$

The boundary condition at $r = 0$ arises due to symmetry, and at $r = R$ corresponds to a constant gas phase atmosphere around the particle, caused by a step change.

Equations (5) [or (6a)] and (7) can be solved to determine the concentration profile in the particle at any time t. These concentration profiles can be integrated to give the overall uptake in the particle:

$$M_t = \frac{3}{R^3} \int_0^R M r^2 \, dr \tag{8}$$

where

$$M = a_p q + \varepsilon_p C.$$

From eq. (8), M_t/M_∞ can be calculated, where M_∞ is the overall uptake in the particle at $t \to \infty$, and is given by

$$M_t/M_\infty = \left\{ \frac{3}{R^3} \int_0^R q \left[a_p + \frac{\varepsilon_p}{b(q_m - q)} \right] r^2 \, dr \right\} \Bigg/ \left\{ q^* \left[a_p + \frac{\varepsilon_p}{b(q_m - q^*)} \right] \right\}. \tag{9}$$

The model equation along with the boundary and initial conditions were solved by a three-level finite-difference scheme [see Lapidus and Pinder (1982)].

EXPERIMENTAL

The uptake of n-hexane on BPL activated carbon was measured by gravimetric measurement using a microbalance. Helium was bubbled through a saturator containing n-hexane in the feed stream. The saturated helium stream was then mixed with a pure helium stream to get a stream containing the desired hexane concentration. The helium–n-hexane stream was passed over the adsorbent sample, and the weight gain by the adsorbent was measured as a function of time. The details of equipment set-up and experimental procedure are given elsewhere (Yeh and Yang, 1989).

RESULTS AND DISCUSSION

The model presented here was used to study the effects of various variables on the overall uptake and intraparticle concentration profiles. The variables studied included the relative contributions of the gas phase and adsorbed-phase diffusivities, isotherm nonlinearity, the gas phase concentration surrounding the particle, and temperature. In all cases the model was solved for constant (average) surface diffusivity as well as for concentration-dependent surface diffusivity, and a comparison is presented to determine the effect of including concentration-dependent surface diffusivity. Moreover, the model was used to calculate the concentration-dependent surface diffusivity of *n*-hexane on carbon at two temperatures, and the surface diffusivities were compared with those calculated from the constant-diffusivity model.

Parameters used and ranges covered for parametric studies

Adsorption of *n*-hexane on activated carbon was taken as the base case in the parametric studies. The Langmuir isotherm parameters for the hexane–activated carbon system at 298 K were $q_m = 0.2208$ g/g (2.567×10^{-10} mol/cm^2) and $b = 529.9$ atm^{-1} (1.273×10^7 cm^3/mol). The surface area (a_p) and intraparticle void fraction (ε_p) for activated carbon were 700 m^2/g and 0.61, respectively. The pellet density for the activated carbon used was 0.85 g/cm^3. The above data were measured in our laboratory (Kapoor, 1989). An initial estimate of the value of D_s for hexane on activated carbon was obtained by the correlation given by Sladek *et al.* (1974) and the heat of vaporization was 7.525 kcal/mol. The calculated value of D_s was of the order of 10^{-5} cm^2/s, depending on the value of the tortuosity factor for the activated carbon. The value of D_g for hexane was calculated by applying the molecular weight correction to the Knudsen diffusivities given in the literature (Doong and Yang, 1986). The calculated value of D_g was 1.788×10^{-5} cm^2/s. The radius of the pellet was equivalent to 12–30-mesh. For parametric study the values of q_m, a_p, ε_p and the radius of the pellet were kept constant, whereas D_g/D_s, b, q^*/q_m, and temperature were varied. Based on the D_s and D_g values given above, the parameter D_g/D_s was varied from 0.1 to 10 to study the relative contribution of the surface and gas phase diffusivities. Parameter b was varied from 1.273×10^6 to 1.273×10^8 cm^3/mol, whereas q^*/q_m was varied from 0.7 to 0.9. Finally, the effect of temperature was studied by using the temperature dependence of b, D_g and D_s, and assuming that the activation energy of surface diffusion and energy of adsorption are related as suggested by Gilliland *et al.* (1974) and Sladek *et al.* (1974). The temperatue was varied from 273 to 323 K.

Comparison between the concentration-dependent surface diffusivity model (CDSDM) and the constant (average) surface diffusivity model (CSDM)

The effect of the concentration-dependent surface diffusivity on the overall uptake and the adsorbed-phase intraparticle concentration profiles was studied by comparing the results for the CDSDM and the CSDM. The system studied was the adsorption of hexane on activated carbon. The parameter values for D_g, D_g/D_s, q_m, b and q^*/q_m were 1.788×10^{-5} cm^2/s, 1.0, 2.567×10^{-10} mol/cm^2, 1.273×10^7 cm^3/mol and 0.9, respectively. The comparison of the overall uptake curve and intraparticle adsorbed-phase concentration profiles are shown in Fig. 1(a) and (b), respectively. It is seen that the effect of using the concentration-dependent surface diffusivity is to increase the overall uptake. Due to the concentration dependence the value of the surface diffusivity at the particle surface in the CDSDM is higher than the average surface diffusivity value used in the CDSDM. Thus the flux at the particle surface in the CDSDM is higher in comparison with the flux in the CSDM. Therefore the overall uptake given by the CDSDM is higher than that for the CSDM at any given time.

From Fig. 1(b) one can make two observations. Firstly, the concentration profiles corresponding to the concentration-dependent model are higher than the profiles corresponding to the CSDM near the particle surface, whereas the reverse is true near the center of the particle at all times during adsorption. Secondly, the slope of the curves corresponding to the constant-diffusivity model decreases monotonically as r decreases, whereas for the concentration-dependent diffusivity model the curves show a point of inflection.

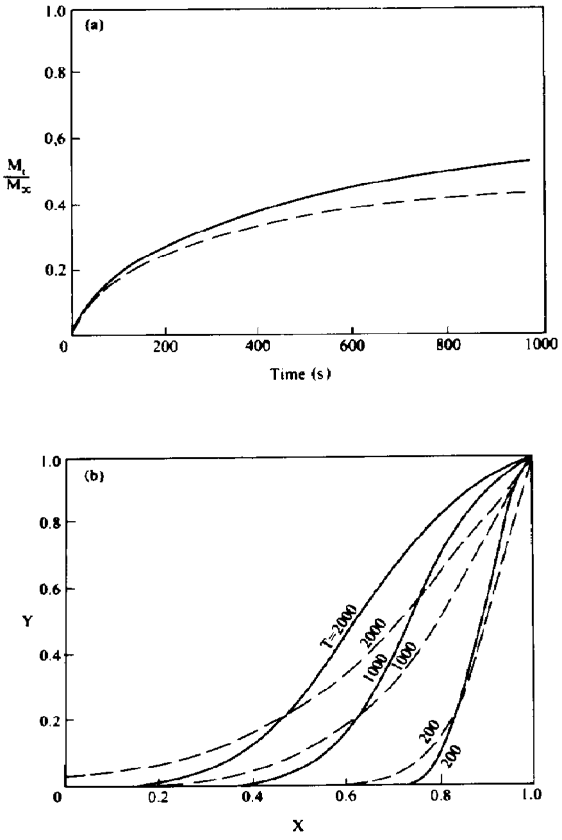

Fig. 1. Adsorption of *n*-hexane in an activated carbon pellet at 298 K. Solid line: prediction by CDSDM. Dashed line: prediction by CSDM. (a) Fractional uptake curves. (b) Adsorbate concentration ($Y = q/q^*$) profiles ($X = r/R$) at various times (in s).

The latter curves show that a higher amount of uptake occurs close to the particle surface due to the higher value of the surface diffusivity, which is in turn due to the higher adsorbed-phase concentration in that region.

Effect of q^*/q_m

Most of the studies in the literature assumed the surface diffusivity to be constant, i.e. the concentration dependence of surface diffusion was not considered. In this study, however, the concentration dependence of the surface diffusivity is considered, and the dependence is described by the HIO model [eq. (4)]. According to the HIO model, the surface diffusivity increases with an increase in the adsorbed-phase concentration, which is consistent with the experimental results reported in the literature (Kapoor *et al*., 1989). However, the HIO model predicts an infinite diffusivity in the limit of $\theta \to 1.0$. There are other models reported in the literature (Kapoor *et al*., 1989) which predict finite diffusivity in the limit $\theta \to 1$. The HIO model, however, is used here due to its mathematical simplicity, and the predictions of the HIO model up to $\theta = 0.9$ are in fair agreement with the experimental results (Kapoor and Yang, 1989). Thus, in this study, the parameter q^*/q_m was varied up to 0.9. The values of q_m, D_g/D_s and b were kept constant at 2.567×10^{-10} mol/cm^2, 1.0 and 1.273×10^7 cm^3/mol, respectively. The overall uptake curves for different values of q^*/q_m are given in Fig. 2 for the CDSDM (solid lines) and CDSM (dashed lines). It is seen that the uptake for the CDSDM is higher than that for the CDSM, and the difference in the two curves is greater for higher values of q^*/q_m. At a higher q^*/q_m value, the surface diffusivity is higher at the particle surface, which in turn increases the surfaces flux into the particle, thus resulting in a greater uptake.

Effect of D_g/D_s

To study the contribution of surface diffusion to the overall intraparticle mass transfer, the parameter D_g/D_s was varied from 0.1 to 10, keeping the values of D_g constant. The values of D_g, q^*/q_m and b were kept constant at 1.788×10^{-5} cm^2/s, 0.9 and 1.273×10^7 cm^3/mol, respectively. The overall uptake curves (Fig. 3) show that a lower value of D_g/D_s significantly lowered the uptake in the particle both for the CDSDM and CSDM. An increase in D_g/D_s from 0.1 to 1 increased the time to reach 50% uptake by more than 10 times. Similar trend was also seen for further increase in D_g/D_s.

It is clearly seen that for n-hexane adsorption in activated carbon at 298 K, surface diffusion contributed significantly to the overall intraparticle mass transfer, and a small change in the surface diffusivity had a large effect on the overall uptake in the particle.

Effect of isotherm non-linearity

The Langmuir isotherm is characterized by two parameters, q_m and b. The parameter q_m is a measure of the saturated amount adsorbed, whereas b is related to the energy of adsorption. The value of b is also associated with the non-linearity of the isotherm. A small value of b corresponds to a fairly linear isotherm, and as the value of b increases the isotherm generally becomes more non-linear. A very high value of b corresponds to a nearly rectangular isotherm. Figure 4 shows the effect of b on the isotherm over a two orders of magnitude variation in b value. Curve 2 corresponds to the hexane isotherm on activated carbon at 298 K. Curves 1 and 3 correspond to isotherms with b values of 1.273×10^8 and 1.273×10^6 cm^3/mol, respectively. The range of b values selected here is typically encountered for various hydrocarbon–activated carbon systems. The parameter C_o is a concentration arbitrarily chosen as 1.4985×10^{-7} mol/cm^3.

To study the effect of isotherm non-linearity on the overall uptake, the value of b was varied from 1.273×10^6 to 1.273×10^8 cm^3/mol, keeping the values of q^*/q_m, D_g/D_s and D_g constant at 0.9, 1.0 and 1.788×10^{-5} cm^2/s, respectively. The overall uptake

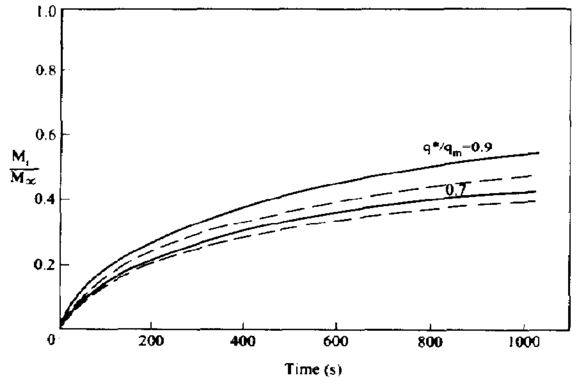

Fig. 2. Effect of ambient concentration (measured by q^*/q_m) on the uptake rate. Solid lines: concentration-dependent surface diffusivity. Dashed curves: constant average surface diffusivity.

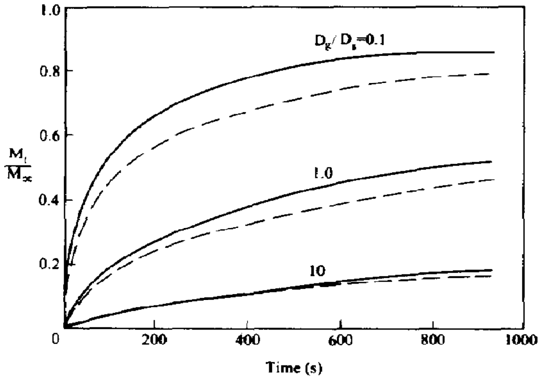

Fig. 3. Effect of surface diffusivity on n-hexane uptake in activated carbon at 298 K. Pore diffusivity (D_g) is fixed. Solid curves: concentration-dependent D_s. Dashed curves: constant average D_s.

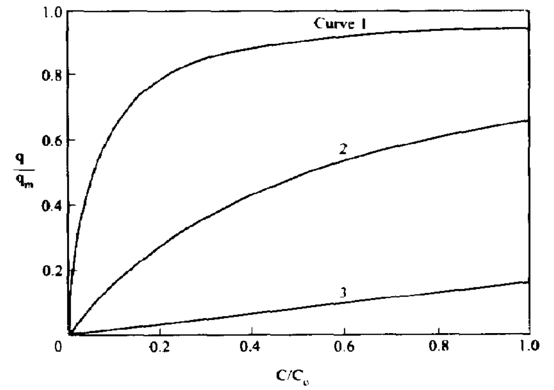

Fig. 4. Langmuir isotherms with different Langmuir constants (b): curve 2 is for n-hexane on activated carbon at 298 K; curves 1 and 3 are obtained by increasing and decreasing, respectively, b by a factor of 10.

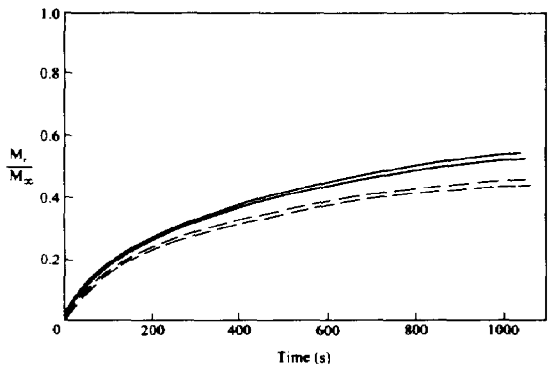

Fig. 5. Effect of isotherm nonlinearity on uptake rates. The upper and lower curves correspond to curves 1 and 3, respectively, in Fig. 4. Solid curves: concentration-dependent D_s. Dashed curves: constant average D_s.

curves predicted by the two models for the two extreme values of b (1.273×10^6 and 1.273×10^8 cm^3/mol) are shown in Fig. 5. The curve corresponding to $b = 1.273 \times 10^7$ cm^3/mol was between the two corresponding curves for each model. It is seen that the change of two orders of magnitude in the b value had only a slight effect on the uptake curve. Similar results were also shown by Leyva-Ramos and Geankoplis (1985). They used a Freundlich isotherm for equilibrium adsorption, and found that by changing the value of exponent from $n = 1$ (linear isotherm) to $n = 5$ (non-linear isotherm) the change in the concentration decay curve was only slight. It should be noted, however, that in the present study the boundary condition, q^*, is kept constant for studies with different values of b. To maintain the value of q^* constant, the gas phase concentration surrounding the particle is greater for a smaller value of b. Moreover, the overall uptake curves predicted by both models are higher for lower values of b, i.e. the linear isotherm results in a higher uptake compared to a non-linear isotherm.

Effect of temperature

The gas phase and adsorbed-phase diffusion, as well as the equilibrium adsorption, are dependent on temperature. The Langmuir parameter, b, is related to temperature by

$$b = \frac{b_o \exp(\varepsilon/RT)}{\sqrt{T}} \tag{10}$$

where ε is the energy of adsorption, and b_o is a constant. The other Langmuir parameter, q_m, is kept constant at 2.567×10^{-10} mol/cm^2. The gas phase diffusivity (assumed Knudsen diffusivity) is related to temperature by

$$D_g = D_{go}(T)^{1/2} \tag{11}$$

where D_{go} is a constant. The surface diffusivity is also a function of temperature and is given as

$$D_s = D_{so} \exp(-E/RT) \tag{12}$$

where E is the activation energy of surface diffusion. It has been suggested (Gilliland *et al.*, 1974) that the activation energy of surface diffusion, E, is related to the energy of adsorption, ε, and the relationship is given as

$$E = a\varepsilon \tag{13}$$

where a is a constant, the value of which depends on the adsorbate–adsorbent system. On correlating data on various systems, Sladek *et al.* (1974) found that $a = 1$ or $1/2$ for physically adsorbed species, depending on the type of bond between the adsorbate and adsorbent. In this work, we present a parametric study for both $a = 1$ and $\frac{1}{2}$. The temperature was varied from 273 to 323 K. To calculate the values of D_s and b at various temperatures from our experimental values at 298 K, it was assumed that the heat of adsorption is equal to the heat of vaporizaton of hexane (7.25 kcal/mol). This assumption will give a lower bound of the temperature dependence, since the heat of vaporization is the lower bound for heat of adsorption. The values of D_g at three temperatures, 273, 298 and 323 K, were 1.7118×10^{-5}, 1.788×10^{-5} and 1.8961×10^{-5} cm^2/s, respectively. The corresponding values of b at the three temperatures were 4.082×10^7, 1.273×10^7 and 4.740×10^6 cm^3/mol, respectively.

For $a = 1$, the values of D_s were 5.826×10^{-6}, 1.788×10^{-5} and 4.612×10^{-5} cm^2/s, respectively, at the three temperatures. From the values given above, it is seen that the variation in the D_g value with temperature was only slight, whereas the D_s value changed significantly. It is also seen that D_g and D_s increased, whereas the value of b decreased with an increase in temperature. Using these values of the parameters the overall uptake curves were calculated by the two models at the three temperatures and the uptake curves are given in Fig. 6. It is seen that an increase in temperatue resulted in a significantly higher uptake curve.

For $a = \frac{1}{2}$, the values of D_s were 1.021×10^{-5}, 1.788×10^{-5} and 2.872×10^{-5} cm^2/s, respectively,

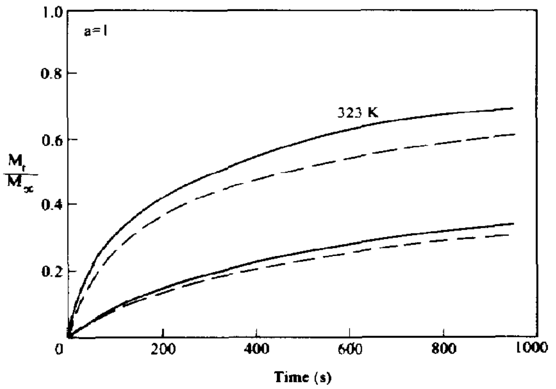

Fig. 6. Effect of temperature (upper: 323 K, lower: 273 K) on uptake rates of *n*-hexane in activated carbon. Activation energy for D_s = heat of adsorption. Solid curves: concentration-dependent D_s. Dashed curves: constant average D_s.

at the three temperatures. It is seen that the variation in D_s value with temperature, for the case of $a = \frac{1}{2}$, is less significant compared to the case of $a = 1$. The other parameters were the same as used in the case of $a = 1$. The overall uptake curves showing the effect of temperature for $a = 1/2$ are given in Fig. 7. It can be seen that the increase in temperature, for $a = 1/2$ also, resulted in an increased uptake. However, on comparison of Figs 6 and 7 it is seen that the change (increase) in uptake with temperatue for the case of $a =,1$ is more than for the case of $a = 1/2$.

Comparison of CDSM and CDSDM on desorption

All the discussion so far has been concerned with the uptake in a particle exposed to a step change in the gas phase concentration. The gas phase and adsorbed-phase concentrations in the particle at time $t = 0$ were zero. In this section we report the results on the desorption of a saturated particle exposed to helium (zero concentration of adsorbate). Comparisons of results from the two models for the total uptake curve and the intraparticle adsorbed-phase profiles are shown in Fig. 8(a) and (b), respectively. The particle was assumed to be saturated so that the initial conditions were

$$\text{at } t = 0 \qquad q = 0.9q^* \qquad \text{for } 0 \leqslant r \leqslant R.$$

After time zero, the particle is exposed to helium; thus, the corresponding boundary conditions are

$$\text{at } r = 0 \qquad \frac{\partial q}{\partial r} = 0$$

$$r = R \qquad q = 0 \qquad \text{for } t > 0.$$

The following parameter values were used: $D_g = 1.788 \times 10^{-5}\ \mathrm{cm^2/s}$, $D_g/D_s = 1$, $q_m = 2.567 \times 10^{-10}\ \mathrm{mol/cm^2}$ and $b = 1.273 \times 10^7\ \mathrm{cm^3/mol}$. It is seen from Fig. 8(a) that the desorption rate is greater for the CSDM compared to that predicted by the CDSDM. This is due to the fact that in the CSDM the value of the surface diffusivity at the particle surface is greater, thus resulting in a greater surface flux. So the effect of concentration-dependent surface diffusivity is to enhance uptake in the adsorption experiment, whereas it decreases the rate of M_f/M_∞ in a desorption experiment. A comparison of the intraparticle adsorbed-phase concentrations predicted by the two models as given in Fig. 8(b) shows that near the particle surface the slope of adsorbed-phase concentration curve is greater for the CSDM. However, the curve corresponding to the CSDM flattens faster near $r = 0$. The comparisons given in Fig. 8(a) and (b) show that inclusion of concentration dependence of surface diffusivity affects both the overall uptake curves and the intraparticle concentration profiles for the case of desorption.

Experimental results and their interpretation

The uptake curves were measured for *n*-hexane on BPL activated carbon at two temperatures (298 and 323 K) using a microbalance. The conditions for the experiments were chosen such that q^*/q_m was approximately 0.9, to ensure the applicability of the HIO model. To adjust the partial pressure of *n*-hexane in the gas stream, the saturated helium stream was mixed with the pure helium in a known ratio. The partial pressures of the hexane were 0.017 and 0.045 atm at 298 and 323 K, respectively.

The uptake data obtained were correlated by the two models: the CSDM and CDSDM. The adsorption parameters discussed earlier were used directly. The values of other parameters such as D_g, ε and a_p were the same as reported earlier. The values of D_{so} and $\bar{D}_s$ were varied for the CDSDM and CSDM to give the best fit of the experimental uptake data. From the $\bar{D}_s$ value for the CSDM, the D_{so} value was evaluated. A comparison of experimental data and the CDSDM fit is given in Fig. 9. The experimental data at very short times was not used for comparison due to the lack of reliability of such data with the gravimetric technique. The values of D_{so} (D_s in the limit of zero loading) obtained from the correlation of experimental uptake data with the CDSDM were

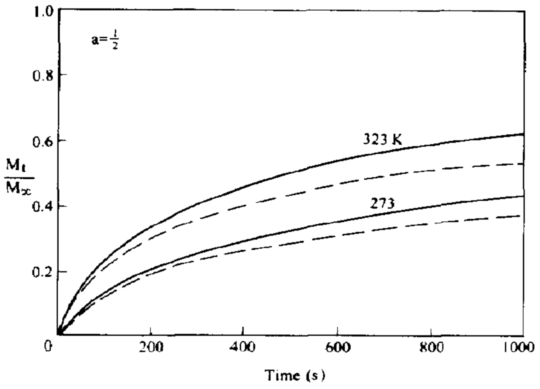

Fig. 7. Same as for Fig. 6, except that activation energy for D_s = half heat of adsorption.

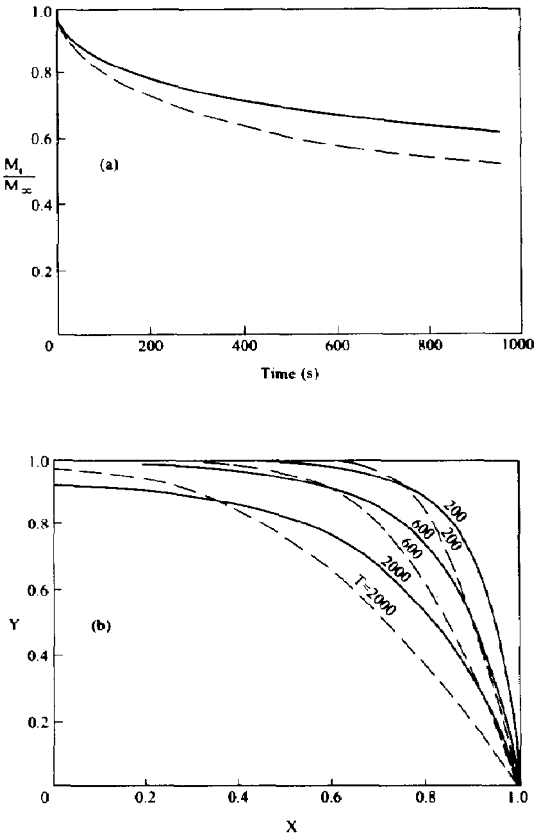

Fig. 8. Desorption of *n*-hexane from activated carbon at 298 K. Solid curves: concentration-dependent D_s. Dashed curves: constant average D_s. (a) Fractional desorption rate. (b) Adsorbate concentration (Y) vs radial distance (X) at different times (t in s).

1.04×10^{-4} and $2.91 \times 10^{-4}\,\mathrm{cm}^2/\mathrm{s}$ at 298 and 232 K, respectively. The same experimental data when correlated by the CSDM gave D_{so} values of 2.2×10^{-4} and $5.97 \times 10^{-4}\,\mathrm{cm}^2\,\mathrm{s}$ at 298 and 232 K, respectively. In calculating the D_{so} values with the constant-diffusivity model, $\bar{D}_s$ was first calculated and eq. (6b) was then used to calculate D_{so}. In this fashion, the D_{so} values calculated from the concentration-dependent and constant-diffusivity models could be compared on the same basis. The comparison showed that the model ignoring the concentration dependence of surface diffusivity predicts higher values of surface diffusivity by a factor of 2–3.

The two values of D_{so} obtained by the CDSDM at two temperatures were correlated by eq. (12) to calculate the activation energy of the surface diffusion of *n*-hexane on BPL activated carbon. The activation energy of surface diffusion was found to be 8.5 kcal/mol, which is higher than, but near, the heat of vaporization of 7.25 kcal/mol. This comparison indicates that the heat of adsorption is close to the activation energy for D_s. Alternatively, since the temperature dependence of the isotherm was accurately measured, the above comparison would indicate that the temperature dependence of pore diffusion (D_g) was underestimated, resulting in the overestimation of the temperature dependence of D_s. D_g was assumed to be proportional to $T^{1/2}$, as in Knudsen diffusion. Involvement of molecular diffusion would have enhanced the temperatue dependence of D_g.

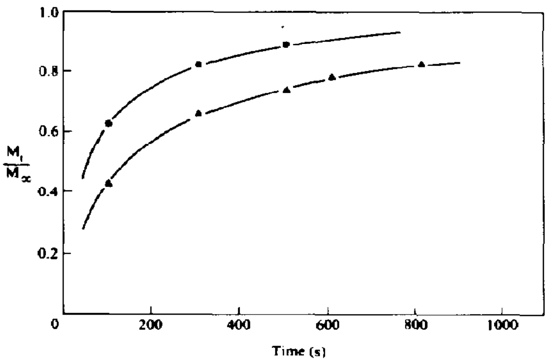

Fig. 9. Uptake curves for *n*-hexane on BPL activated carbon. Points: experimental, lines: CDSDM. Lower: 298 K, upper: 323 K.

CONCLUSION

(1) It was shown, for adsorption/desorption of *n*-hexane on activated carbon, that surface diffusion contributes significantly to the overall intraparticle mass transfer, and the concentration dependence of surface diffusion affects significantly both the overall uptake rates and the intraparticle concentration profiles.

(2) Due to the concentration dependence of surface diffusivity, it was shown that the gas phase concentration affects the dimensionless uptake curve (M_t/M_∞ vs time), which would not be true if surface diffusion was independent of concentration.

(3) The overall effect of the concentration dependence of surface diffusion is to enhance the uptake during adsorption and reduce it during desorption.

(4) On correlating the experimental uptake data of *n*-hexane on BPL activated carbon, it was found that the model ignoring the concentration dependence of the surface diffusivity yielded higher values of the surface diffusivity by a factor of 2–3.

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NOTATION

a_p	surface area per unit volume of particle
b	Langmuir isotherm parameter
b_o	constant
C	gas phase concentration in pores

C_o	an arbitrary value of C, taken as 1.4985×10^{-7} mol/cm^3
D_g	gas phase diffusivity
D_s	surface diffusivity
D_{so}	surface diffusivity in the limit of zero loading
E	activation energy of surface diffusion
M	total amount (gas phase and adsorbed phase) at radial position r
M_t	total uptake at time t
M_∞	total uptake at infinite time
N_r	total flux at a radial position r
q	adsorbed-phase concentration or amount adsorbed, on a per surface area basis
q_m	amount adsorbed corresponding to monolayer, or saturated amount
q^*	amount adsorbed in equilibrium with the gas surrounding the particle
r	radial position in the particle
R	radius of particle or gas constant
t	time
T	temperature
X	radial distance (r/R)
Y	adsorbate concentration (q/q^*)

Greek letters

α	defined by eq. (5)
β	defined by eq. (5)
γ	a_p/ε_p
ε	energy of adsorption
ε_p	intraparticle void fraction
θ	fractional surface coverage or q/q_m

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