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Gas sorption kinetics by differential closed-loop recycle method: Effect of heat of adsorption

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Abstract An analytical mathematical model is used to investigate the influence of minute adsorbent temperature changes on the kinetics of sorption of a gaseous adsorbate from mixture with a carrier gas using a differential closed loop recycle method. Isothermal operation may not be achieved even when a very high gas circulation rate is used. Very small changes in the adsorbent temperature during the process can cause substantial departure from isothermal uptake behavior. It is shown that the kinetic process can be assumed to be isothermal only for trace adsorbate concentrations. A criterion for validity of isothermal data analysis is proposed.

Keywords Ad(de)sorption · Kinetics · Equilibrium · Non-isothermal · Closed-loop recycle

Introduction

Conventional batch methods for measurement of gas ad(de)sorption kinetics like the gravimetric, the volumetric, and the frequency response techniques generally require non-isothermal models for data analysis. This is because the heat of ad(de)sorption can not be removed (supplied) from (to) the adsorbent fast enough to maintain the system isothermal during the ad(de)sorption process unless the kinetics of sorption is extremely slow. Differential adsorption tests, where the changes in the adsorbate loading and the temperature in the sorbent are deliberately kept very small, have been designed and practiced to simplify the non-isothermal model analysis. This allows linearization of the changes in the equilibrium amount adsorbed due to changes in the gas phase adsorbate concentration and adsorbent temperature as well as decoupling of the effects of these two variables. Consequently, analytical solutions of non-isothermal ad(de)sorption kinetic models using different sorption mechanisms can be obtained to facilitate data analysis. Examples include (i) differential constant pressure gravimetric tests for a pure adsorbate involving mass transfer by Fickian Diffusion models (neglecting or including the thermal resistance within the adsorbent particle) (Ruthven, 1984; Haul and Stremming, 1984) or Linear Driving Force (LDF) models (neglecting or including the thermal resistance within the adsorbent particle) (Sircar, 1983; Sircar and Kumar, 1984), (ii) differential constant pressure gravimetric tests for binary adsorbates with mass transfer by LDF model (Sircar, 1994), and (iii) differential frequency response test for a pure adsorbate using a bi-porous adsorbent (combined micropore and macropore diffusion) (Sun et al., 1994) or an adsorbent with combined micropore and surface barrier resistances (Sun and Meunier, 1993).

The closed-loop recycle method of measuring sorption equilibria and kinetics facilitates removal or supply of heat from or to the adsorbent mass inside the

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test apparatus by re-circulating the entire gas phase in the system over the adsorbent. The gas stream continuously enters the adsorption vessel at the temperature of the thermostated system (T_o), and it leaves the vessel at a slightly higher or lower temperature. It is cooled down or heated up to temperature T_o before it re-enters the vessel.

The experimental protocol for the differential closed- loop recycle method consists of (i) equilibrating a small themostated mass of an adsorbent with a mixture of an adsorbate gas (mole fraction $= y^\circ$) and a carrier gas (single or multi-component) at pressure P_o (atm)and temperature T_o (K), (ii) slightly changing the gas phase adsorbate composition (mole fraction $= y^s$) at time $t = 0$, and (iii) circulating the gas at P_o and T_o over the adsorbent until a new equilibrium state for the adsorbate (mole fraction $= y^\infty$) is reached. A uniform gas phase adsorbate composition [$y(t)$ at time t] in the entire system as well as a uniform adsorbent temperature [$T(t)$ at time t] in the adsorbent vessel can be maintained by using a high recirculation rate (very small residence time in the adsorber) and reducing the gas mixing time. The equilibrium amount adsorbed at P_o, T_o and y^∞ and the sorption kinetics during the process can be evaluated by measuring the transient gas phase composition [$y(t)$] in the system. Adsorption or desorption kinetics can be studied by selecting a value of $y^s > y^\circ$ or $y^s < y^\circ$, respectively.

Figure 1 shows a schematic drawing of a closed-loop recycle apparatus which was used for measuring equilibrium and kinetics of adsorption of Freon-12 at infinite dilution (Golden and Sircar, 1994). The key parts include (i) an adsorbent chamber, (ii) a gas circulating pump, (iii) a main gas circulation loop, (iv) a by-pass loop and (v) an online continuous gas analyzer. The entire apparatus is enclosed in a constant temperature air bath at T_o. The by-pass loop is used to change the gas phase adsorbate concentration of the main loop at the start of each experiment. A continuous gas analyzer (mass spectroscope) was used to monitor the gas phase Freon concentration with time. A detailed description of the experimental protocol can be found elsewhere (Golden and Sircar, 1994).

The purpose of this work is to develop an analytical mathematical model of the differential closed-loop recycle experiment for evaluating the influence of adsorption heat on sorption kinetics. A specific objective is to establish a criterion under which isothermal analysis of the kinetic data can be justified.

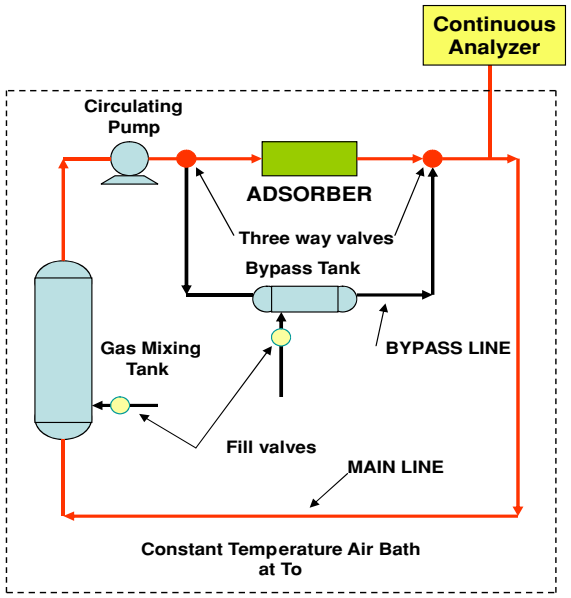

Fig. 1 Schematic drawing of a closed-loop recycle apparatus

Mathematical model

It is assumed that the adsorbent chamber is a cylinder (Internal diameter = D, cm; Length = L, cm; Internal cross sectional area = A = $\pi D^2/4$, cm^2) which is packed with w gms of the adsorbent particles (radius = R_P, cm, bulk density = ρ_b, g/cc, void fraction = ε). The void volumes (cc) of the packed adsorbent chamber, the main loop, and the by-pass loop are, respectively, V_A, V_M, and V_B. The specific equilibrium adsorbate loadings (moles/g) at P_o, T_o and adsorbate gas mole fractions of y°, y^∞ are, respectively, n° and n^∞. The specific equilibrium adsorbate loading (moles/g) corresponding to the gas phase at $y(t)$, P_o and $T(t)$ is $n^*(t)$. A mass balance for the adsorbate in the closed system yields:

$$N(t) = [\alpha y(t) + n(t)] = N^\circ = [\alpha y^s + n^\circ] = N^\infty = [\alpha y^\infty + n^\infty] \quad (1)$$

where $N(t)$, N°, and N^∞ are, respectively, the total specific amounts (moles/g) of the adsorbate gas in the system at time t, at the start of the experiment ($t = 0$), and at equilibrium ($t \to \infty$). Equation (1) shows that these parameters are equal and constants during the test. The variable α [$= P_o V^S / wRT_o$] is the total specific amount (moles/gm) of gas in volume V^S ($= V_A + V_M$), which is the combined void volume of the main loop

and the adsorbent chamber. $n(t)$ is the specific amount (moles/gm) of the adsorbate gas adsorbed at time t. R is the gas constant.

Equilibrium amount adsorbed

It follows from Eq. (1) that the specific equilibrium capacity (n^{∞}) of the adsorbate at P_o, T_o, and y^{∞} is simply given by:

$$n^{\infty} = \alpha(y^s - y^{\infty}) + n^{\circ} \tag{2}$$

The entire adsorption isotherm for the adsorbate gas $[n^{\infty} = f(P_o, T_o, y^{\infty})]$ from a given composition of the carrier gas can be generated by repeating the experiments (constant P_o and T_o) starting with a clean adsorbent (n°, $y^{\circ} = 0$) and progressively increasing the values of y^s at the start of the experiments. Adsorption reversibility can also be checked by carrying out desorption experiments.

Non-isothermal ad(de)sorption kinetics

It also follows from Eq. (1) that the rate of ad(de)sorption of the adsorbate and the specific amount adsorbed $[n(t)]$ at time t are given by:

$$\frac{dn(t)}{dt} = -\alpha y(t); \quad [n(t) - n^0] = -\alpha[y(t) - y^S] \tag{3}$$

For a differential test, the specific equilibrium capacity $[n^*(t)]$ of the adsorbate gas at P_o, T(t), and y(t) is given by (isotherm linearization and thermodynamics) (Sircar, 1983):

$$\begin{aligned}[n^*(t) - n^0] &= aP_o[y(t) - y^0] + b\theta; \\ a &= \left[\frac{\partial n^*}{\partial p}\right]_T; b = \left[\frac{\partial n^*}{\partial T}\right]_p \\ &= -\left[\frac{aP_o y^0 q^0}{RT_0^2}\right]\end{aligned} \tag{4}$$

where p $(=Py)$ is the partial pressure of the adsorbate gas, and $\theta(t)$ $[=\{T(t) - T_o\}]$ is the change in the adsorbent temperature at time t. $T(t)$ is the adsorbent temperature at time t. The value of $\theta(t)$ is very small for a differential test. The variables a (>0) and b (<0) are, respectively, the partial pressure and temperature coefficients of the adsorbate equilibrium isotherm evaluated at the initial equilibrium conditions (P_o, T_o, and y°) of the test. q° (cal/mole) is the isosteric heat of adsorption of the adsorbate gas at n° and T_o.

For a non-isothermal ad(de)sorption process, θ is equal to zero at the start of the experiment ($t = 0$), then it increases (decreases), goes through a maximum (minimum) value, and finally approaches zero when the new equilibrium state is reached ($t \to \infty$). Consequently, it follows from Eqs. (2) and (4) that:

$$\begin{aligned}(n^{\infty} - n^{\circ}) &= aP_o(y^{\infty} - y^{\circ}) = \alpha(y^s - y^{\infty}); \\ [n(t) - n^{\circ}] &= \alpha[y^s - y(t)]; \\ f(t) &= \frac{n(t) - n^o}{n^{\infty} - n^o} = \frac{y^s - y(t)}{y^s - y^{\infty}}\end{aligned} \tag{5}$$

where $f(t)$ is the fractional uptake of the adsorbate at time t. It can be calculated by experimentally measuring y^s, y^{∞} and $y(t)$.

The heat balance for the adsorbent mass at time t may be written as:

$$\begin{aligned}\frac{d\theta(t)}{dt} &= -\lambda\theta + \psi\frac{dn(t)}{dt}; \\ \lambda &= \left[\frac{AQC_g + a_{ex}h}{wC_S}\right] = \left[\frac{QC_g}{LC_S\rho_b} + \frac{4h}{DC_S\rho_b}\right]; \\ \psi &= \left[\frac{q^o}{C_S}\right]\end{aligned} \tag{6}$$

where Q is the molar flow rate (moles/cm^2/sec) of the circulating gas based on empty cross sectional area (A) of the adsorbent chamber. C_g (cal/mole/K) and C_S (cal/gm/K) are, respectively, the specific heat capacities of the circulating gas and the solid adsorbent. The variables a_{ex} $(=\pi$DL, cm$^2)$ and h (cal/cm^2/sec/K) are, respectively, the external heat transfer area of the cylindrical adsorbent chamber and the effective heat transfer coefficient for heat loss from the adsorbent to the air bath. The variable λ (sec^{-1}) is the effective heat transfer coefficient for heat removal from the adsorbent by convection and through the chamber wall. It was assumed in writing Eq. (6) that the adsorbent and the gas phases were in thermal equilibrium at all times.

It is assumed that the Linear Driving Force (LDF) model describes the ad(de)sorption rate of the adsorbate gas. The model is mathematically simple and most

frequently used in adsorptive process design (Sircar and Hufton, 2000):

$$\frac{dn(t)}{dt} = k[n^*(t) - n(t)] \tag{7}$$

where k ($\sec^{-1}$) is the LDF mass transfer coefficient for the adsorbate gas at a loading of n° and temperature T_o. Equations (6) and (7) can be combined to get

$$\frac{d^2\theta(t)}{dt^2} + [\lambda + k(1+\beta-b\psi)]\frac{d\theta(t)}{dt} + k\lambda(1+\beta)\theta(t) = 0; \quad \beta = \left[\frac{aP_o}{\alpha}\right] \tag{8}$$

Equation (8) can be integrated to obtain analytical expressions for fractional uptake, $f(t)$, of the adsorbate gas and the adsorbent temperature, $\theta(t)$, as functions of time (t) using the appropriate boundary conditions [$f(t\to 0) = 0$, $f(t\to\infty) = 1$, and $\theta(t\to 0, \infty) = 0$]:

$$f(t) = \frac{[n(t) - n^0]}{[n^\infty - n^0]} = \frac{B}{\lambda\sqrt{A^2 - 4B}}\left\{\left[\frac{\lambda + r_2}{r_2}\right][1 - \exp(r_2 t)] - \left[\frac{\lambda + r_1}{r_1}\right][1 - \exp(r_1 t)]\right\} \tag{9}$$

$$\theta(t) = \frac{\psi\Delta(n^0)}{\lambda}\left\{\frac{B}{\sqrt{A^2 - 4B}}\right\}[\exp(r_1 t) - \exp(r_2 t)] \tag{10}$$

The key variables of Eqs. (9) and (10) are given by:

$$A = [\lambda + k(1+\beta-b\psi)]; \quad B = k\lambda(1+\beta);$$
$$r_1 = \frac{-A + \sqrt{A^2 - 4B}}{2}; \quad r_2 = \frac{-A - \sqrt{A^2 - 4B}}{2}$$

where r_1 and r_2 are the roots of the second order ordinary differential Eq. (8).

The maximum (or minimum) value of θ(t) profile is θ_m. It occurs at $t = t_m$:

$$\theta_m = \frac{\psi\Delta(n^0)}{\lambda}\left\{\frac{B}{\sqrt{A^2 - 4B}}\right\} \times \left[r_1\left(\frac{r_2}{r_1}\right)^z - r_2\left(\frac{r_2}{r_1}\right)^{z-1}\right],$$
$$z = \frac{r_1}{r_1 - r_2}; \quad t_m = \frac{\ln(r_2/r_1)}{r_1 - r_2} \tag{11}$$

The variable $\Delta[= (\frac{n^\infty - n^0}{n^0}) = \frac{aP_o(y^\infty - y^0)}{n^0}]$ in Eqs. (10) and (11) represents the net fractional change in the adsorbent loading of the adsorbate gas during the differential test. The equilibrium adsorbate gas mole fraction (y^∞) at the end of the test is given by:

$$y^\infty = \frac{y^S + y^0\beta}{1+\beta} \tag{12}$$

Equation (12) can provide guide lines for selection of y^S for a given set of y° and β values in order to obtain a desirable value for y^∞.

Equation (9) can be used to estimate the adsorbate mass transfer coefficient (k) from the experimental uptake data, $f(t)$, by specifying the physical dimensions of the adsorption system (D, L, w, R_P, ρ_b, ε, V_A and V_M), the experimental test conditions [T_o, P_o, Q], and the physical and adsorptive properties of the test system [C_g, C_s, k_g, μ_g, h, $n^*(p,T)$, q°]. Equation (10) can then be used to calculate the system temperature [$\theta(t)$] as function of time.

Special case of isothermal system

For a truly isothermal ad(de)sorption process, where $\{n^*(t) - n^\circ\} = aP_o\{y(t) - y^\circ\}$, Eqs. (3), (5) and (7) can be combined and integrated to obtain:

$$f(t) = \frac{n(t) - n^0}{n^\infty - n^0} = 1 - \{\exp[-k(1+\beta)t]\} \tag{13}$$

Equation (13) shows that a plot of $\ln[1 - f(t)]$ against t will be a straight line with a slope equal to $[-k(1+\beta)]$. The slope depends on the adsorbate mass transfer coefficient (k), the adsorbate gas partial pressure gradient of the equilibrium isotherm (a) at n° and T_o, the system pressure (P_o), the system temperature (T_o), and the specific void volume of the closed-loop system (V^S/w).

Approximate isothermal uptake behavior

It can be shown that the variables of Eq. (9) simplify to [$A \sim \{\lambda + k(1 + \beta)\}$], [$\sqrt{(A^2 - 4B)} \sim [\lambda - k(1 + \beta)]$; [$r_1 \sim -k(1 + \beta)$, $r_2 \sim -\lambda$], and Eq. (9) approximately reduces to Eq. (13) under the following condition:

$$\frac{-b\psi}{(1+\beta)} = + \frac{aP_o y^o (q^o)^2}{C_S R (T_o)^2 [1+\beta]} << 1 \tag{14}$$

The criterion (14) is generally satisfied when the adsorbate gas concentration is very low ($y^\circ << 1$, trace level, ppm). In other words, isothermal analysis of uptake data from a differential closed-loop recycle sorption test may be justified only for sorption of adsorbate gases in trace concentrations.

The previously mentioned publication on measurement of adsorption equilibria and kinetics of Freon-12 at infinite dilution by a closed-loop recycle method (Golden and Sircar, 1994) satisfied criterion (14). The sorption uptake curves followed Eq. (13), indicating that the sorption process was isothermal. It should be mentioned here that the expression used for the isothermal uptake curve [Eq. (6) in Golden and Sircar (1994)] has a different form but it is identical with Eq. (13) above. Furthermore, the kinetic tests in Golden and Sircar (1994) were conducted within the linear Henry's law region ($a = K$, Henry's law constant at T_o) of the adsorption isotherm of Freon-12. Thus, a differential change in adsorbate gas concentration was not necessary for isotherm linearization since the process was isothermal.

Non-isothermal sorption uptake by closed-loop recycle method—a case study

Criterion (14) indicates that the sorption uptake by the differential closed-loop recycle method can not be assumed to be isothermal unless y° is very small. The effect of the heat of adsorption on the fractional uptake curve was examined by using Eqs. (9) and (10) for sorption of 5.0 mole % C_2H_6 from inert Helium on 5 A zeolite at 323 K (T_o) and a total gas pressure of 1.0 atm (P_o). The equilibrium adsorption isotherm for C_2H_6 on the zeolite can be described by the Langmuir model (Ruthven and Loughlin, 1972; Sircar and Kumar, 1983):

$$n^* = \frac{mcP_o y^o}{1 + cP_o y^o}; c = c^* \exp(q^\circ / RT_o);$$
$$a = \frac{mc}{[1 + cP_o y^o]^2} \tag{15}$$

where n^* (moles/g) is the equilibrium amount adsorbed at temperature T_o (K). P_o (atm) is the total gas pressure and y° is the gas phase mole fraction of the adsorbate. m (moles/g) is the saturation adsorption capacity for the adsorbate and q° (cal/mole) is the isosteric heat of adsorption. c (atm^{-1}) is the Langmuirian gas-solid interaction parameter, and c^* (atm^{-1}) is a constant. The variable a (moles/gm/atm) is the adsorbate partial pressure ($p = P_o y_o$) gradient, $[\frac{\delta n^*}{\delta p}]_T$, of the isotherm at T_o.

The Langmuir model parameters for adsorption of C_2H_6 on 5 A zeolite were (Sircar and Kumar, 1983): $m = 1.4 \times 10^{-3}$ moles/g ; $c^* = 5.97 \times 10^{-6}$ atm^{-1} ; $q^\circ = 8800$ cal/mole. Thus, the value of the parameter c at 323 K was 5.38 atm^{-1}. The LDF mass transfer coefficient for adsorption of C_2H_6 from helium on 5 A zeolite beads ($R_P = 0.1505$ cm, $\rho_b = 0.7$ gms/cc, $C_S = 0.22$ cal/g/K) at 323 K was: $k = 0.023 - 0.07$ sec^{-1}. It was estimated by analysis of a column break through data (Ruthven and Loughlin, 1972) for adsorption of dilute C_2H_6 from helium using the LDF kinetic mechanism (Sircar and Kumar, 1983). The properties of the helium gas at 1.0 atm and 323 K were: $C_g = 5.0$ cal/mole/K, viscosity $\mu_g = 5.19 \times 10^{-3}$ moles/cm/sec, thermal conductivity $\kappa_g = 3.77 \times 10^{-4}$ cal/sec/cm/K (Vargaftik, 1975).

It was assumed that the adsorbent chamber was cylindrical [$L = 3.0$ cm, $D = 1.0$ cm, $w = 1.65$ gms, $\varepsilon = 0.72$] and the combined void volume of the packed adsorbent chamber and the main loop was 300 cc/g (V^S/w). The adsorbent was initially equilibrated with 5.0% C_2H_6 (y°) in helium at P_o and T_o. The gas phase C_2H_6 mole fraction was then changed by 5.0% [$=\{(y^s - y^\circ)/y^\circ\} \times 100$] at the start of the experiment. The heat loss through the walls of the adsorbent chamber was assumed to be controlled by the internal surface of the chamber. Thus, h could be calculated by the following correlation by Leva (Ruthven, 1984; Leva, 1949):

$$[hD/\kappa_g] = 0.813[\mathrm{Re}]0.19 \exp\{-12R_P/D\};$$
$$\mathrm{Re} = 2R_P Q/\mu_g \tag{16}$$

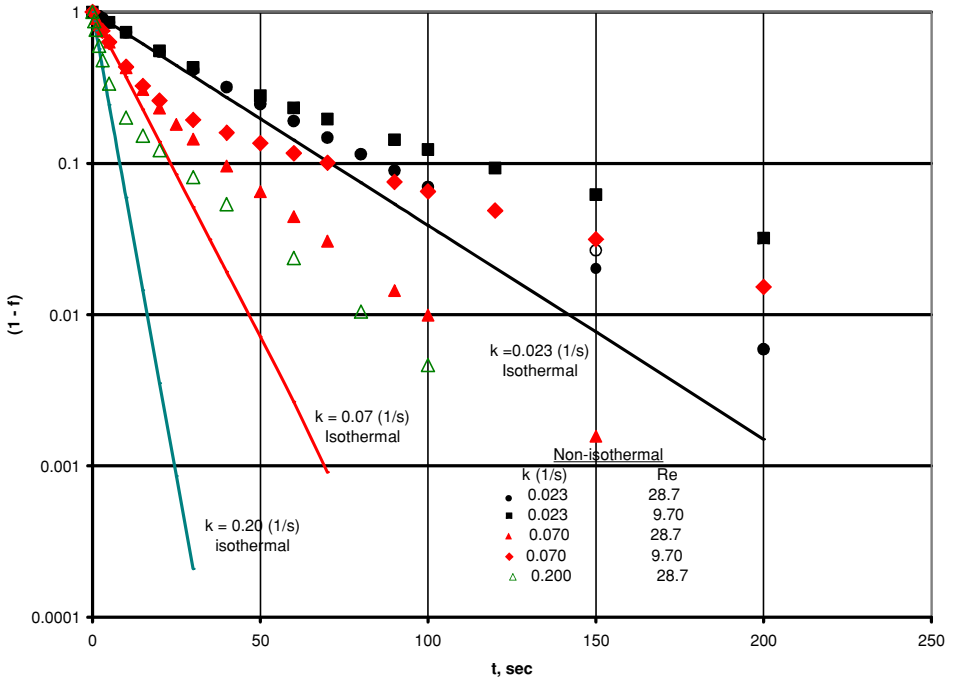

Fig. 2 Model uptake curves by differential closed-loop recycle method

where Re is the particle Reynolds number for gas flow through the adsorbent chamber.

The primary parameters of Eqs. (9) and (10) were estimated for this system to be: $a = 4.66 \times 10^{-3}$ moles/g/atm, $\alpha = 1.13 \times 10^{-2}$ moles/g, $\beta = 0.412$, $\psi = 4.0 \times 10^4$ g · K/mole, $\Delta = 0.0279$, and $\{-b\psi/(1 + \beta)\} = +0.28$. Thus criterion (14) was not satisfied. These parameters were used to generate the $f(t)$ and $\theta(t)$ profiles for circulating gas flow rates of 100 cc/sec [$Q = 4.81 \times 10^{-3}$ moles/cm^2/sec, Re = 28.7, $\lambda = 0.0545$ sec^{-1}] and 33.3 cc/sec [$Q = 1.60 \times 10^{-3}$ moles/cm^2/sec, Re = 9.6, $\lambda = 0.0193$ sec^{-1}] in conjunction with the LDF mass transfer coefficients (k) of 0.023, 0.07 and 0.20 sec^{-1}.

Figures 2 and 3 show the results of the model calculations. The sorption uptake profiles are plotted as ln [1 − $f(t)$] against t in Fig. 2. The corresponding $\theta(t)$ profiles are plotted in Fig. 3. The values of the parameters (k and Re) are given in the figures.

The linear plots in Fig. 2 represent isothermal uptakes [Eq. (13)] for different k values. The corresponding non-linear uptake curves in Fig. 2 at different gas flow rates are caused by non-isothermal adsorption described by Fig. 3. The most interesting and important point is that a very small change in the adsorbent temperature (Maximum value: $\theta_m \sim 0.1-0.2$ K) can cause a significant departure from isothermal uptake behavior for a system where the isosteric heat of adsorption is moderately large. This is because of the fact that the driving force for mass transfer of the adsorbate gas at any time t for a non-isothermal differential test, $[n^*\{T(t)\} - n(t)]$, can be substantially lower than that for the corresponding isothermal case, $[n^*\{T_o\} - n(t)]$, even when the adsorbent temperature changes are small. It has been shown that the difference between non-isothermal and isothermal uptakes for a constant pressure differential adsorption test can be significant due to a very small change in the adsorbent temperature (Sircar, 1981). The same behavior is encountered by all differential adsorption tests mentioned earlier (Ruthven, 1984; Haul and Stremming, Sircar, 1983, 1984; Sircar and Kumar, 1984; Sun et al., 1994; Sun and Meunier, 1993). Figure 2 also shows that the non-isothermal effect is amplified when the mass transfer coefficient is high, the gas circulation rate is low, and the isosteric heat of adsorption is high (not studied in this work), as expected.

Such a small change in the adsorbent temperature (Fig. 3) may be difficult to measure. It can be easily ignored and the assumption of isothermal uptake can be

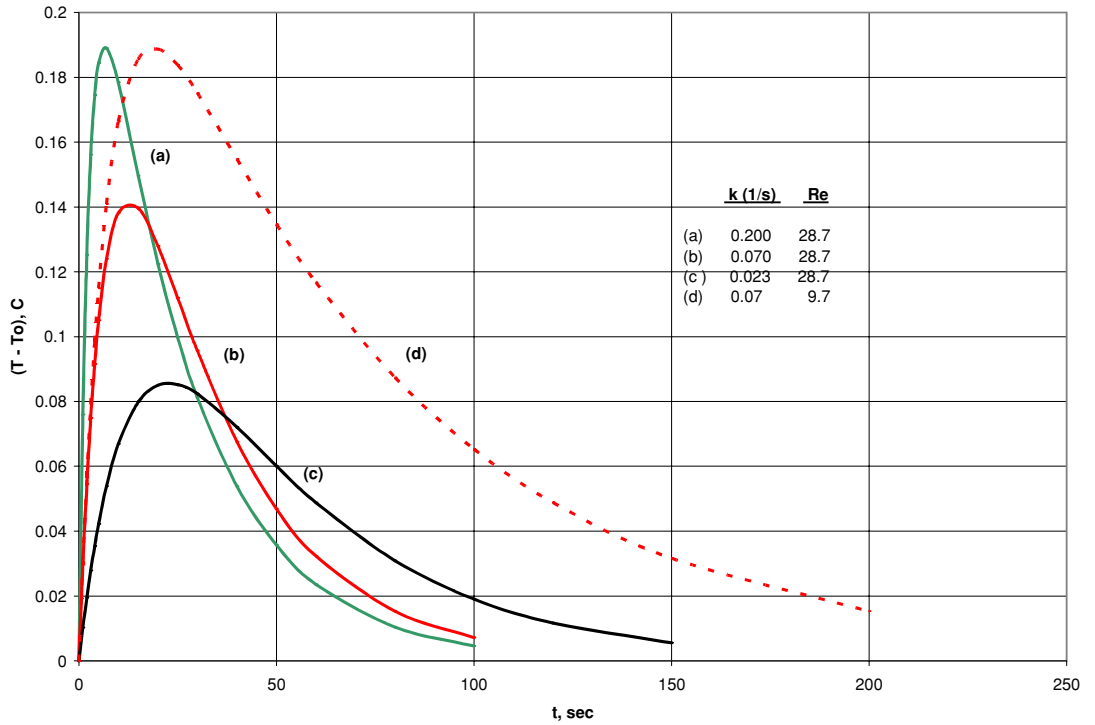

Fig. 3 Adsorbent temperature changes during uptake process

made. However, that will lead to very misleading data interpretation. Two most common errors are (i) calculation of a smaller value for the mass transfer coefficient than actual (slower kinetics than actual), and (ii) assumption of a more complex kinetic mechanism model than LDF, such as multiple mass transfer resistances, to describe the uptake data.

The study also shows that it may not be possible to remove the heat of adsorption from the adsorbent as soon as it is produced even when a very high gas flow rate (100 cc/sec, Re ∼29) is used. This is particularly true when the adsorbate mass transfer coefficient is large (open triangles in Figs. 2, and 3a). The heat removal from the adsorbent is primarily controlled by convection. Thus, the gas flow rate has a pronounced effect on the non-isothermal uptake curves (closed triangles and diamonds in Figs. 2, 3b and d) for a given value of k. The thermal effects become less pronounced when the mass transfer coefficient is small and the gas flow rate is high (closed circles in Figs. 2 and 3c), but true isothermal behavior can be assumed only when the criterion (14) is satisfied.

The closed-loop recycle method can be very convenient for measurement of sorption equilibria and kinetics of a single or multi-component trace adsorbates from mixtures with a single or multi-component carrier gas provided that the criterion of Eq. (14) is satisfied. That will permit simple and unambiguous analysis of isothermal uptake data by the test. Furthermore, if the measurements are carried out within the Henry's law region of the adsorbate isotherm, the requirement of a differential test can be relaxed because the isotherm is already linear and the process is isothermal (for trace adsorbates).

Nomenclature

A	empty cross-section area of adsorbent chamber, variable of Eqs. (9) and (10)
a_{ex}	external heat transfer area of the adsorbent chamber
a	$[\frac{\delta n^*}{\delta p}]_T$ defined by Eq. (4)
B	variable of Eqs. (9) and (10)
b	$[\frac{\delta n^*}{\delta T}]_p = -[\frac{aP_o y^o q^o}{RT_o^2}]$ defined by Eq. (4)
c	Langmiur gas-solid interaction parameter, Eq. (15)
c^*	constant, Eq. (15)
C_g	specific heat capacity of gas phase

C_s specific heat capacity of the adsorbent
D diameter of the adsorbent chamber
f(t) $\frac{[n(t)-n^o]}{[n^\infty-n^o]}$ = fractional uptake at time t
h effective heat transfer coefficient between adsorbent chamber and outside bath
k effective adsorbate mass transfer coefficient
k_g gas thermal conductivity
L length of the adsorbent chamber
$N(t)$ total specific moles of adsorbate gas (constant) in the system at time t
N° total specific moles of adsorbate gas in the system at the start of experiment
N^∞ total specific moles of adsorbate gas in the system at the end of the experiment
n° specific adsorbate loading in equilibrium with gas phase at y°, P_o and T_o
n^∞ specific adsorbate loading in equilibrium with gas phase at y^∞, P_o and T_o
n*(t) specific adsorbate loading in equilibrium with gas phase at $y(t)$, P_o and $T(t)$
$n(t)$ specific amount of adsorbate adsorbed at time t
P_o total gas pressure (constant) in the system
p(t) partial pressure of the adsorbate at time $t = P_o$y(t)
Q molar flow rate of the circulating gas
q° isosteric heat of adsorption of the adsorbate gas at n° and T_o
R_P radius of the adsorbent particle
r_i roots of Eq. (8)
R gas constant
Re $2R_P Q/\mu_g$, Reynolds Number
T(t) system temperature at time t
T_o system temperature at start and end of experiment
V_A void volume of adsorbent chamber
V_B void volume of by-pass loop
V_M void volume of main loop
V^S ($V_A + V_M$)
w amount of adsorbent particles in the system
y(t) gas phase mole fraction of adsorbate at time t
y° adsorbate mole fraction of saturating gas before the start of the experiment
y^∞ adsorbate mole fraction of the gas at the end of experiment
y^s gas phase adsorbate mole fraction at the start of the experiment

Greek symbols

α $[P_o V^S/wRT_o]$
β $[aP_o/\alpha]$ defined by Eq. (8)
Δ $[(n^\infty - n^\circ)/n^\circ] = [aP_o(y^\infty - y^\circ)/n^\circ]$
ε helium void fraction of packed adsorbent column
$\theta(t)[T(t) - T_o]$
ρ_b adsorbent bulk density
ψ $[q^\circ/C_s]$ defined by Eq. (6)
λ $[\frac{QC_g}{LC_S\rho_b} + \frac{4h}{DC_S\rho_b}]$ defined by Eq. (6)
μ_g gas viscosity

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