ELSEVIER

Journal of Chromatography A, 873 (2000) 39–51

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Kinetics of solid-phase extraction and solid-phase microextraction in thin adsorbent layer with saturation sorption isotherm

Semen N. Semenov*[,1], Jacek A. Koziel, Janusz Pawliszyn*[,2]

Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1 Canada

Received 28 August 1999; received in revised form 24 December 1999; accepted 27 December 1999

Abstract

The effects of sorbent saturation in thin adsorbent layers have been much overlooked in earlier research and should be taken into account in both the theory and practice of solid-phase extraction (SPE) and solid-phase microextraction (SPME). The adsorption kinetics of a single analyte into a thin adsorptive layer was modeled for several cases of agitation conditions in the analyzed volume. The extraction process in the adsorbent layer was modeled using a Langmuir isotherm approximated by the linear isotherm at low concentrations and by a saturation plateau at concentrations exceeding the critical saturation concentration. Laplace transformations were used to estimate the equilibration time and adsorbed analyte concentration profile for no agitation, practical and perfect agitation in the analyzed volume. The equilibration time may be significantly reduced at high degrees of oversaturation and/or agitation in the analyzed volume. The resulting models indicated that the adsorbent layer becomes saturated at some critical value of the oversaturation degree parameter. The critical value of the oversaturation parameter is affected by both the concentration of the analyte in the analyzed volume and the sorbent characteristics. It was also shown that the adsorption process is carried out via the propagation of the saturation adsorption boundary toward the inner boundary of the adsorbent layer. These new adsorption models should serve as ''stepping stones'' for the development of competitive adsorption kinetic models for both SPE and SPME, particularly in cases where fast sampling is used.

Keywords: Adsorption isotherms; Mathematical modeling; Solid-phase microextraction; Solid-phase extraction; Kinetic studies; Sorbent saturation

1. Introduction

Solute partitioning between a liquid or gas and a thin, solid or liquid sorbent layer is widely used in many scientific and technological applications, including analyte extraction/sample preparation in solid-phase extraction (SPE) and solid-phase microextraction (SPME). For SPE, a high-affinity sorbent retains and concentrates organic compounds from a dilute liquid or gaseous phase. These compounds are later desorbed and introduced into a chromatograph or other analytical device. Limitations to SPE (mainly due to its large adsorbent layer) have been addressed by SPME [1], which since its

*Corresponding authors.

E-mail addresses: sem@fly.triniti.troitsk.ru (S.N. Semenov), janusz@uwaterloo.ca (J. Pawliszyn)

[1]On leave from the Institute of Biochemical Physics, Russian Academy of Science, Kosygin Street 4, 117977 Moscow, Russia. Fax: +7-095-137-4101.

[2]Tel.: +1-519-888-4641; fax: +1-519-746-0435

0021-9673/00/$ – see front matter
PII: S0021-9673(99)01338-2

introduction in the early nineties has found many applications [2]. For SPME, a thin layer of high-affinity solid (or liquid for absorptive extraction/pre-concentration) sorbent is coated on the surface of a fused-silica fiber. Analytes partition to the sorbent and are later transferred to an analytical instrument, e.g. gas chromatograph, for sample desorption, separation and quantification. This method minimizes the extraction/sample preparation time and allows for the same sorbent coating to be reused after each sample extraction/injection/desorption cycle.

In a typical adsorptive SPME extraction analytes diffuse from the analyzed volume onto the sorbent layer. To enhance analyte uptake, partition constant values for the sorbents used in commercially available SPME typically range from 10^3 to 10^5 [1]. However, sorbents with high partition constants may be quickly saturated even at relatively low analyte concentrations, due to the limited number of available adsorption sites. Typical specific surface areas for the solid adsorbents range between 10^2 and 10^3 $m^2\ g^{-1}$ [3]. The molecule size and the adsorption site area may be as low as approximately 10^{-9} m and 10^{-18} m^2, respectively. Thus, the maximum concentration of adsorption sites available in these sorbents cannot exceed 10^{20}–10^{21} g^{-1}. Considering an average partition constant of approximately 10^4, these sorbents may be saturated at analyte concentrations of 10^{16}–10^{17} g^{-1}, i.e., from 0.1 to 1 ppm. Larger molecules, e.g. greater than five characteristic atomic sizes, have an even smaller number of available adsorption sites, and the critical concentration for sorbent saturation may be lower, ranging from 10 to 100 ppb. As such, sorbent saturation can be reached for typical SPME applications, and its kinetics has not been fully addressed in the existing literature.

A comprehensive theory of extraction by absorption-type SPME coatings was presented by Pawliszyn [1]. Recently, Ai developed a theoretical description of non-equilibrium absorption into SPME coatings [2,4–6]. These models can be used to estimate mass of analytes absorbed with SPME, when achieving equilibrium extraction for quantification purposes requires an inconveniently long time. Gorecki et al. developed a steady-state theory for analyte extraction via adsorption by selected porous polymer fibers [7]. To date, there is no comprehensive SPME theory for including competitive dynamic adsorption processes. Such processes are very important in cases where very short sampling times are used, e.g. less than 10 s, and where the quantification is based on molecular gas-phase mass transfer coefficients [8]. Adsorption kinetics including displacement effects are well understood in processes involving protein sorption [9,10]. However, the time scale for protein adsorption is often an order of magnitude greater than those used in fast sampling with SPME [11].

Sorbent saturation is much different from the ''linear'' extraction regime. First, the time necessary for establishing equilibrium between the adsorbed and free analytes should depend on the analyte concentration in the analyzed volume, since only a part of the total amount of analyte can be adsorbed in the saturation regime. For the same reason, the final concentration distribution and the amount of the analyte adsorbed should not depend on its concentration in the analyzed volume, and should be controlled by the adsorbent capacity only. Secondly, analyte ''outflow'' from the free to the bound (adsorbed) form, where it could not move across the adsorbent layer, should lead to slower observable diffusion. Thirdly, mass transfer conditions should affect the equilibration process, e.g. the degree of agitation in the analyzed gas or liquid may control the boundary layer thickness in a sample volume. Finally, there is a potential for reversible binding and the ''displacement'' of lower-molecular-mass analytes by higher-molecular-mass compounds.

In addition, competitive adsorption has been observed in SPME practice (Fig. 1). The effects of saturation and competitive adsorption in thin adsorbent layers were not fully taken into account in previous theoretical developments of SPE/SPME [1,2]. A full understanding of this process is crucial for expanding SPE/SPME applications to very complex analyte sample matrices. Thus, there is a growing need for models describing saturation effects and competitive adsorption in thin adsorbent layers for commercially available SPME fibers.

In this research, the kinetics of single analyte adsorption into a thin layer during SPE and SPME was modeled. Several limiting cases of extraction/mass transfer were considered. Laplace transformations were used to estimate the analyte concentration

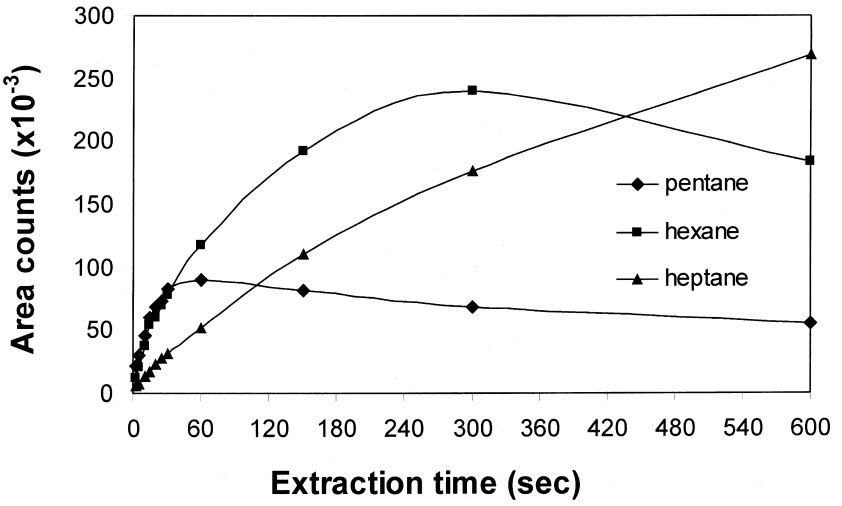

Fig. 1. Competitive adsorption for gas phase *n*-alkanes on a polydimethylsiloxane–divinylbenzene fiber.

time profiles for no agitation, typical and perfect agitation conditions in a sample volume. The extraction kinetics were modeled in an adsorbent layer with the saturation sorption isotherm approximated by the linear isotherm at low concentrations and by a saturation plateau at concentrations exceeding the critical saturation concentration. The resulting models are based on several physicochemical and extraction parameters, and should serve as a basis for the development of new models for competitive adsorption in thin, solid or semi-solid-phases.

2. Theoretical development

2.1. Formulation of the mathematical problem

The concentration distribution of an analyte in a given volume (outside of sorbent layer) is commonly described using a diffusion equation based on Fick's second law. This relationship can be reduced to one dimension assuming that for a thin adsorbent layer, e.g. SPME, adsorptive coating curvature can be neglected:

$$\frac{\partial c_e}{\partial t} = D_e \cdot \frac{\partial^2 c_e}{\partial x^2} \quad (1)$$

where c_e is the analyte concentration in the analyzed volume, D_e is the diffusion coefficient of the analyte in the analyzed volume, t is the time, and x is the transverse coordinate in the adsorption layer. The initial condition to Eq. (1) has the form

$$c_e(t=0) = c_0 \quad \text{at } x \leq 0 \quad (2)$$

The boundary condition to Eq. (1) depends on the agitation regime. Several analyte concentration distributions in the analyzed volume near the adsorbent layer for several limiting cases of agitation are presented in Fig. 2. Eq. (1) describes the analyte concentration with no agitation conditions, where no means are employed to agitate gas or liquid in the analyzed volume (the no agitation regime in Fig. 2). The opposite case is represented by conditions of perfect agitation, where the concentration distribution is always uniform and does not depend on the analyte outflow onto the adsorbent layer (the perfect agitation regime in Fig. 2). In typical SPME applications, some means for agitation are used, and uniform analyte concentration exists in the analyzed volume outside a thin boundary layer with constant thickness δ determined by the agitation conditions (the practical agitation regime in Fig. 2). The analyte concentration inside the boundary layer changes linearly with the distance, i.e. decreasing toward the boundary with the adsorbent layer [1].

Inside the sorbent layer, i.e. between the outside

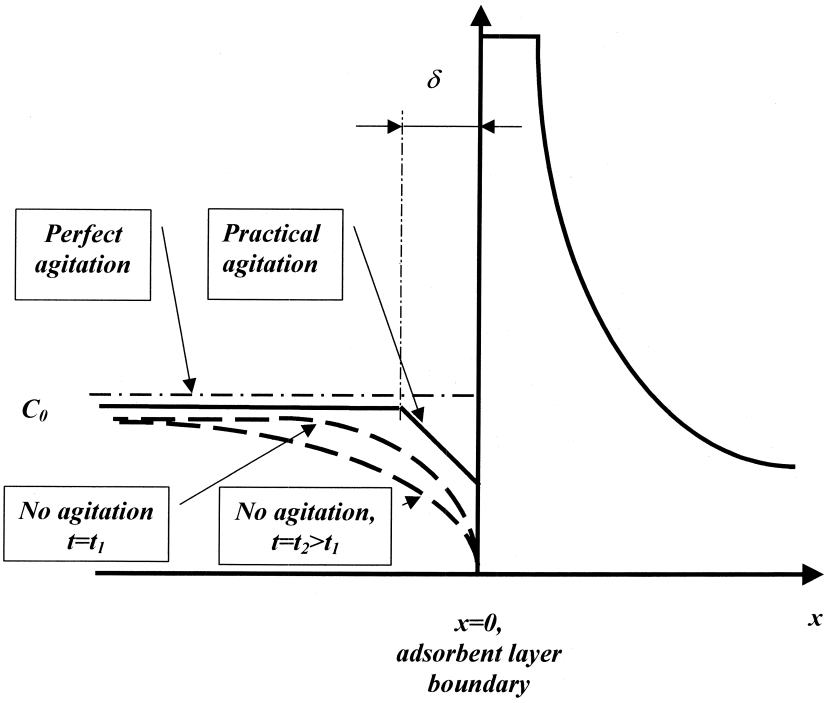

Fig. 2. Concentration distribution of the analyte in the vicinity of the adsorbent layer boundary.

and inside boundary of a sorbent, the analyte concentration distribution is described by the following equation [3]

$$\frac{\partial c_i}{\partial t} + \frac{\partial q}{\partial t} = D_i \cdot \frac{\partial^2 c_i}{\partial x^2} \tag{3}$$

where c_i is the concentration of the free analyte in the adsorption layer, q is the concentration of the bound (adsorbed) solute, and D_i is the diffusion coefficient of the free analyte in the adsorption layer. The initial boundary conditions may be described by initial extraction into pure adsorbent layer and the condition of the wall impermeability at the inner boundary of the adsorbent layer

$$c_e(t = 0) = 0 \quad \text{at } x > 0 \tag{4}$$

and

$$\frac{\partial c_i}{\partial x} = 0 \quad \text{at } x = h \tag{5}$$

where h is the adsorbent layer thickness. It was assumed that a very thin saturation layer is already present at the external boundary of the adsorbent layer. However, the initial saturated layer is extremely thin compared to the adsorption layer width, and it is established almost instantaneously (see Appendix A).

The diffusion and sorption of an analyte in Eq. (3) can be solved if $q(c)$, also identified as the adsorption isotherm, is known. The simplest form of this adsorption isotherm can be described by the Langmuir isotherm [3]

$$q(c) = \frac{q_s kc}{q_s + kc} \tag{6}$$

where q_s is the maximum concentration of the adsorbed solute at saturation and k is the sorbent partition constant. The adsorption isotherm was assumed to be the sum of two parts

$$q(c) = kc \quad \text{at } c \leq \frac{q_s}{k} \tag{7}$$

and

$$q(c) = q_s \quad \text{at } c > \frac{q_s}{k} \tag{8}$$

This approach allows for the consideration of two separate regions in the adsorbent layer, i.e. saturation region, and non-saturation region, respectively (Fig. 3). A transition between these two regions occurs, when the free analyte concentration in the adsorbent layer reaches its critical value $c_s = q_s/k$. Furthermore, this approach simplifies the adsorption model to the class of problems with moving boundaries [12]. The time dependence of the moving boundary coordinate $x_0(t)$ between the aforementioned regions can be described by the equation

$$c_i(x_0, t) = \frac{q_s}{k} \tag{9}$$

The adsorption layer becomes completely saturated for

$$x_0(t_{eq}) = h \tag{10}$$

i.e., the saturation boundary approaches the inner boundary of the adsorption layer. The adsorption layer saturation time (t_{eq}), also known as the equilibration time, can be estimated by solving Eq. (10). Similarly, the approximation of the adsorption isotherm by Eqs. (7) and (8) reduces the mathematical problem to solving Eq. (3) in the saturated region.

In addition, this approach allows one to model cases where a single analyte or several analytes are extracted and adsorbed to different adsorption sites. In the case where several analytes are extracted and compete for the same adsorption sites, a similar approach should be coupled with the examination of the displacement process kinetics.

For analyte concentrations low enough to consider the linear adsorption isotherm, Eq. (3) reduces to

$$\frac{\partial c_i}{\partial t} = \frac{D_i}{1+k} \cdot \frac{\partial^2 c_i}{\partial x^2} \tag{11}$$

where the parameter $D_i/(1 + k)$ represents the effective analyte diffusion coefficient which accounts for the analyte adsorption/desorption in the sorbent layer. This effective diffusion coefficient should be relatively small for a strong adsorbent, i.e. for $k \gg 1$. Lower effective diffusion is common in chromatography [12], where peak broadening may occur due to diffusion combined with the adsorption/desorption in a column coating.

The diffusion equation for the free analyte in the saturation region has the form

$$\frac{\partial c_i}{\partial t} = D_i \cdot \frac{\partial^2 c_i}{\partial x^2} \tag{12}$$

The typical distribution of both free and bound analyte in the adsorbent layer is presented in Fig. 4. The boundary conditions at the sorbent layer/analyzed volume boundary should describe the continuity of the analyte concentration and the analyte flowrate in the direction perpendicular to the boundary. Thus, the first boundary condition can be written simply as

$$c_e(x = 0) = c_i(x = 0) \tag{13}$$

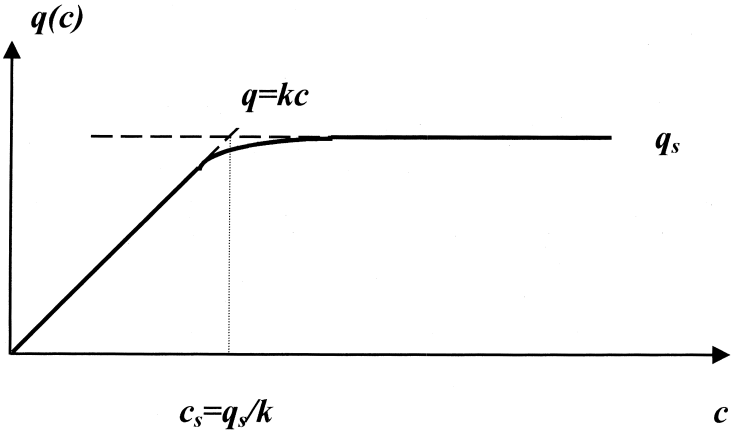

Fig. 3. Langmuir isotherm (solid line) and its approximation in this article (dashed line).

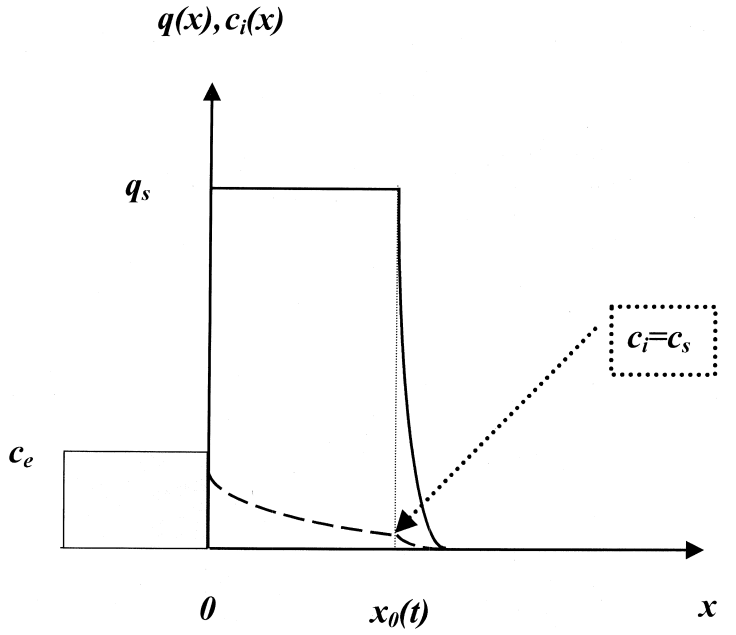

Fig. 4. Distribution of the free (dashed line, c_i) and bound (solid line, q) analyte concentration in the adsorbent layer.

where c_i signifies the analyte concentration in the sorbent pores. The bonded analyte concentration (q_s) remains constant inside the sorbent layer from $x=0$ to $x=x_0(t)$. However, there is analyte flux to the bound (adsorbed) state ($-q_s \partial x_0/\partial t$), related to the motion of the saturation adsorption boundary. Thus, in the saturation region, the second boundary condition may be written in the form

$$D_i \cdot \frac{\partial c_i}{\partial x} + q_s \cdot \frac{\partial x_0}{\partial t} = D_e \cdot \frac{\partial c_e}{\partial x} \quad \text{at } x = 0 \tag{14}$$

Eqs. (1)–(14) completely define the adsorption kinetics into thin layers, assuming that equilibrium exists between the free and bound analytes in the adsorption layer as described by the Langmuir isotherm (Eqs. (6)–(8)). For the case of the perfect agitation regime (Fig. 3), where the diffusion in the analyzed volume is faster than diffusion in the adsorbent layer, i.e. $D_i \gg D_e$, Eq. (14) reflects ideal, uniform analyte concentration in the analyzed volume

$$\frac{\partial c_e}{\partial x} \approx 0 \text{ at } x = 0 \tag{15}$$

For the case of the no agitation regime (Fig. 3), analyte flux is controlled by diffusion only, as described by Eqs. (13) and (14). For the practical agitation regime (Fig. 3), analyte diffusion is present in the depletion layer (δ) only, and the boundary diffusion flow could be written as

$$D_i \cdot \frac{\partial c_i}{\partial x} = -D_i \cdot \frac{A_e}{\delta} \quad \text{at } x = 0 \tag{16}$$

where A_e is the concentration reduction in the depletion layer. Thus, the second boundary condition in the practical agitation regime may be written as

$$-D_i \cdot \frac{A_e}{\delta} + q_s \cdot \frac{\partial x_0}{\partial t} = D_e \cdot \frac{\partial c_e}{\partial x} \quad \text{at } x = 0 \tag{17}$$

Finally, the effects of the analyte concentration distribution in the inner, non-saturated adsorption layer region were neglected. It can be shown that the estimated concentration distribution will affect the equilibration time value only if the saturation boundary motion is very slow. A Laplace transformation was used to solve the aforementioned systems of equations for each agitation regime case

$$c(s, x) = \int_0^\infty c(x, t)\, e^{-st}\, dt \tag{18}$$

where s is the transformation parameter.

2.2. No agitation conditions

For the no agitation regime, the analyte concentration distribution (Eq. (1)) with the initial condition (Eq. (2)) was used. Eqs. (12) and (11) were used for the analyte concentration distribution in the saturated and unsaturated adsorption layer, respectively, with Eq. (4) serving as the boundary condition. Similarly, Eqs. (13) and (14) describe the boundary between the analyzed volume and the adsorbent layer, i.e. at $x=0$. Then, in the Laplace domain, the analyte concentration in the analyzed volume and in the saturation region, respectively, have the following form

$$c_e(x, s) = A_e\, e^{\sqrt{(s/D_e)}x} + \frac{c_0}{s} \tag{19}$$

$$c_i(x, s) = A_i\, e^{-\sqrt{(s/D_i)}x} \tag{20}$$

$$q(x, s) = \frac{q_s}{s} \tag{21}$$

The coefficients A_e and A_i can be found using the boundary conditions, i.e. Eqs. (13) and (14). First, the saturation boundary motion, i.e. Eq. (9) can be described by the following equation in the Laplace domain

$$x_0(s) = \sqrt{\frac{D_i}{s}} \ln y, \tag{22}$$

where

$$y = \frac{kA_i}{q_s} \tag{23}$$

Variable y is the degree of ''oversaturation'' for the analyte in the adsorbent layer and could be estimated as the ratio of the free analyte concentration at the analyzed volume/adsorbent layer boundary to the critical concentration corresponding to the adsorbent saturation. Next, Eqs. (19)–(21) were substituted into Eqs. (13) and (14), resulting in the following equation

$$\left(1 + \sqrt{\frac{D_i}{D_e}}\right) y + k\sqrt{\frac{D_i}{D_e}} \ln y = \frac{y_0}{s}, \tag{24}$$

where

$$y_0 = \frac{kc_0}{q_s} \tag{25}$$

where the parameter y_0 may be defined as the degree of oversaturation in the analyzed volume. Eq. (24) may be further reduced for typical y, y_0 and k values of approximately 10, 10, and 10^3–10^4, respectively,

$$k\sqrt{\frac{D_i}{D_e}} \ln y = \frac{y_0}{s} \tag{26}$$

Eq. (26) can be solved for $\ln y$ and substituted into Eq. (22)

$$x_0(s) = \sqrt{\frac{D_e}{s}} \cdot \frac{y_0}{sk} \tag{27}$$

In the non-saturated adsorbent region, the analyte concentration may be written using Eq. (12)

$$q(x > x_0) = \frac{q_s}{s} \cdot e^{-\sqrt{(sk/D_i)}(x - x_0)} \tag{28}$$

The amount of analyte adsorbed by the sorbent per unit of the boundary surface area (Q) can be expressed as

$$Q(s) = q_s x_0(s) + \int_{x_0}^{\infty} q(x > x_0)\, dx \tag{29}$$

Eq. (29) may be solved using Eqs. (27) and (28)

$$Q(s) = \sqrt{D_i} q_s \cdot \left(\frac{y_0}{k}\sqrt{\frac{D_e}{D_i}} + 1\right) \cdot s^{-3/2} \tag{30}$$

Finally, in the time domain $Q(s)$ can be expressed as

$$Q(t) = 2q_s \cdot \left(\frac{y_0}{k} \cdot \sqrt{\frac{D_e}{D_i}} + 1\right) \cdot \sqrt{\frac{D_i t}{\pi}} \tag{31}$$

Eq. (31) represents the contribution of the adsorbed analyte in both the saturated and non-saturated adsorbent region, when the saturation boundary is far from the internal boundary of the adsorbent layer, i.e. shortly after the initiation of the adsorption process. Eq. (31) may be further simplified for high analyte concentrations and cases where the diffusion in the analyzed volume is much greater than diffusion in the adsorbent layer. In this case, i.e. $(y_0/k)(D_e/D_i)^{1/2} \gg 1$, the contribution of the unsaturated region to extraction may be neglected. Finally,

the equilibration time can be estimated by solving Eqs. (10) and (27)

$$t_{eq} = \frac{\pi}{4D_e} \cdot \left(\frac{q_s}{c_0} h \right)^2 \quad (32)$$

The amount of the adsorbed analyte per unit boundary area is constant and equal to $Q_{eq} = q_s h$, for $t > t_{eq}$.

2.3. Practical agitation conditions

Like to the no agitation condition, Eqs. (1), (2), (11), (12) and (4) were used for the analyte concentration distribution in the analyzed volume, saturated and unsaturated adsorption layer, and initial concentration condition, respectively. In the practical agitation regime, the boundary conditions at $x = 0$, were described by Eqs. (13) and (17). The resulting analyte concentration in the analyzed volume had the following form in the Laplace domain

$$c_e(x = 0, s) = -A_e + \frac{c_0}{s} \quad (33)$$

As in the case of no agitation conditions, in the saturation region, the analyte concentration is described by Eqs. (20) and (21). The saturation boundary motion was described using Eq. (22), and substituted into the boundary conditions, Eqs. (13) and (17), respectively. The resulting expression involving the degree of oversaturation in the adsorbent layer had the following form

$$\left(1 + \frac{\delta\sqrt{D_i s}}{D_e} \right) \cdot y + k \frac{\delta\sqrt{D_i s}}{D_e} \ln y = \frac{y_0}{s} \quad (34)$$

and could be further reduced for typical sorbent characteristics

$$k \cdot \frac{\delta\sqrt{D_i s}}{D_e} \ln y = \frac{y_0}{s} \quad (35)$$

Eq. (35) could be solved for $\ln y$ and substituted into Eq. (22)

$$x_0(s) = \frac{D_e}{\delta} \cdot \frac{y_0}{ks^2} \quad (36)$$

corresponding to the following linear time dependence of the saturation boundary motion

$$x_0(s) = \frac{D_e}{\delta} \cdot \frac{y_0}{k} t \quad (37)$$

As expected, the saturation boundary propagates much faster for the practical agitation regime with a typically thin depletion layer (δ), in comparison to the no agitation regime. The amount of analyte adsorbed by the sorbent per unit of the boundary surface area can be expressed as

$$Q(s) = q_s \cdot \frac{D_e}{\delta} \cdot \frac{y_0}{k} t \quad (38)$$

Similarly, the equilibration time could be estimated using the following equation

$$t_{eq} = \frac{\delta h}{D_e} \cdot \frac{k}{y_0} \quad (39)$$

and the amount of the adsorbed analyte per unit boundary area should be constant and equal to $Q_{eq} = q_s h$, for $t > t_{eq}$.

2.4. Perfect agitation conditions

The hypothetical case of perfect agitation conditions should result in rapid mass transfer and/or the strong oversaturation, i.e.

$$y \gg k \cdot \frac{\delta\sqrt{D_i s}}{D_e} \quad (40)$$

In the case of high oversaturation, the analyte concentration in the analyzed volume (c_0) should be a few orders of magnitude lower than the maximum concentration of the adsorbed analyte q_s. However, a much higher extraction enrichment could be reached in the case of rapid mass transfer and decreased depletion layer thickness even at lower oversaturation degrees. In such a case, $\delta(D_i s/D_e)^{1/2} \ll 1$ and Eq. (34) may be reduced to the form

$$y = \frac{y_0}{s} \quad (41)$$

for $A_i = c_0$. Subsequently, Eq. (10) for the saturation boundary may be written in the form

$$\frac{c_0}{s} \cdot e^{-\sqrt{(sk/D_i)}x} = \frac{q_s}{ks} \quad (42)$$

Eq. (42) corresponds to perfect agitation conditions, where the analyte concentration at the analyzed

volume/adsorbent layer boundary is the same as the analyte concentration in the analyzed volume far from this boundary. Furthermore, the diffusion flow from the analyzed volume to the adsorbent layer is very small.

The saturation boundary motion can be estimated using a Laplace transformation [6]

$$1 - erf\left(\frac{x_0}{\sqrt{D_i t}}\right) = \frac{1}{y_0} \tag{43}$$

Eq. (43) can only be satisfied at very large values of the error function argument, for which the following approximation may be used [13,14]

$$1 - erf(z) \approx \frac{\sqrt{\pi}}{2} \cdot \frac{e^{-z^2}}{z} \tag{44}$$

Thus, the saturation boundary motion can be estimated by substituting Eq. (44) into Eq. (43) and transforming the latter equation to logarithmic form

$$x_0(t) = \sqrt{\ln\left(\frac{\sqrt{\pi}}{2} \cdot y_0\right) \cdot D_i t} \tag{45}$$

Similarly, the equilibration time can be estimated as

$$t_{eq} = \frac{h^2}{\ln\left(\frac{\sqrt{\pi}}{2} \cdot y_0\right) \cdot D_i} \tag{46}$$

Eq. (46) can also be used to evaluate the thickness of the depletion boundary layer δ at perfect agitation conditions. The characteristic values of the parameter s were assumed to be approximately t_{eq}^{-1}, thus

$$\delta \ll \frac{D_e h}{D_i \sqrt{\ln\left(\frac{\sqrt{\pi}}{2} \cdot y_0\right)}} \cdot \frac{c_0}{k} \tag{47}$$

Since the diffusion coefficient in the adsorbent layer may be approximately five to ten times smaller than in the liquid analyzed volume, this condition can be satisfied in samples with much greater analyte concentrations. Thus, for SPME with a y_0/k ratio of approximately 0.1, the maximum value of δ should not be greater than $\delta \approx 0.01\ h$.

The condition equivalent to perfect agitation may also be reached for adsorption from a gas to solid adsorbent impregnated with a liquid, or adsorption to gel-like polymer sorbent. For such conditions the y_0/k ratio should be approximately equal to unity and $(D_i/D_e)^{1/2} \ll 1$.

3. Discussion

The magnitude of the critical analyte concentration in the analyzed volume necessary for the saturation adsorption layer was predicted in all examined agitation conditions. These concentrations were comparable to the typical SPME conditions, where partition constants range from 10^3–10^4. Furthermore, critical analyte concentrations y and y_0 of approximately unity indicate the presence of a transition between saturated and unsaturated extraction. The dependence of the equilibration time on the saturation concentration was also predicted. Such a dependence is observed in experiments and is well-documented in literature [1,2]. As expected, there should be no such dependence in unsaturated conditions. The extraction kinetic profiles for several extraction regimes are illustrated in Fig. 5.

Mass transfer between the analyzed volume and the adsorbent layer is controlled by both the equilibration time and the degree of agitation. For the no agitation regime, mass transfer is controlled by the analyte diffusion near the boundary, and the analyte inflow is decreasing with time, i.e. by $t^{1/2}$, due to the spatial extension of the diffusion depletion layer δ. For practical agitation conditions, mass transfer between the analyzed volume and the adsorbing layer is both steady-state and linear, and is controlled by the degree of agitation only. Thus, the equilibration time may be significantly reduced for the same analyte concentration by increasing the agitation rate, as is often applied in SPME practice [1,2]. This statement can be further illustrated by comparing the equilibration times for no agitation and practical agitation conditions, i.e. Eqs. (32) and (39). For the transition from no agitation to practical agitation, the reduction in equilibration time is approximately $(\delta c_0/hq_s)$. Since the ratio c_0/q_s is very small for typical extraction conditions, even slight agitation should significantly reduce the equilibration time for $\delta \geq h$. Thus, in the saturation regime, the degree of agitation becomes a very important parameter controlling extraction kinetics.

Similarly, the effects of unsaturated and the satu-

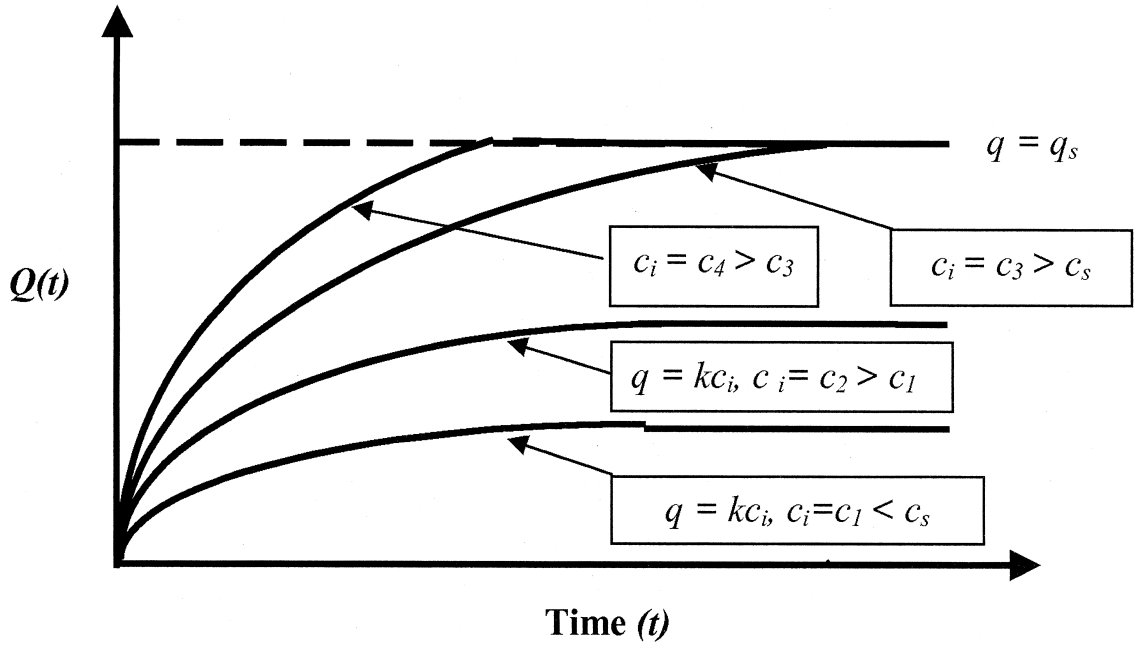

Fig. 5. Extraction kinetics for no saturation ($c_1 = c_1$, $c_2 < c_s$) and saturation conditions ($c_1 = c_3$, $c_4 > c_s$).

rated regime on equilibration times could be examined. For the no saturation regime, the characteristic time necessary to reach the diffusion/adsorption equilibrium in the adsorbent layer can be estimated using Eq. (11). This equilibration time is approximately equal to $(k+1)h^2/D_i$, and does not depend on the boundary conditions. The ratio of the equilibration times for the saturated and unsaturated regimes is approximately equal to $\delta/(hy_0)$, if $D_i/D_e \approx 1$. Thus, the equilibration process is shorter for cases with increased agitation, e.g. $\delta < h$ and/or greater degree of oversaturation. However, it is not necessary to provide a high analyte concentration in the analyzed volume, since a high oversaturation degree may be also reached using a highly effective sorbent. For example, a one or two order of magnitude reduction of the equilibration time should be achieved for cases where the depletion layer thickness (δ) is approximately an order of magnitude less than the adsorbent layer width and the oversaturation degree y_0 ranges from 3 to 10, respectively.

Analyte concentration is another important parameter affecting the equilibration time. For a highly effective sorbent, the analyte concentration should be very low and approximately y_0 times lower than the analyte concentration at the boundary between the analyzed volume and the adsorbent layer. A much shorter time is required to reach such a low analyte concentration at the saturation boundary in comparison to the time necessary to achieve an analyte concentration comparable to its boundary concentration. Furthermore, reaching a low analyte concentration corresponds to the equilibrium in the no saturation adsorption regime. Thus, for a highly effective sorbent, a shorter equilibration time is required and may be facilitated by increased agitation. In the case of the saturated regime, intensive mass transfer at the boundary between the analyzed volume and the sorbent is crucial in providing a fast extraction, similar to perfect agitation conditions. In the case of perfect agitation conditions, where $\delta < 10^{-2} h$ and a high oversaturation degree is achieved, e.g. $y_0 \approx 0.1 k$, the equilibration time should be approximately of the same order as the time of the free analyte diffusion into an adsorbent layer as described by Eq. (46). Thus, perfect agitation conditions may be used to describe a fast extraction with relatively high analyte concentration.

In a typical SPME extraction, saturation adsorption may not be employed for the quantification of the analytes in the analyzed volume. The ultimate amount of the extracted analyte should be equal to $q_s h$ and independent of the analyte concentration in the analyzed volume for the unit surface area of the adsorbent layer. However, the equilibration time itself could be used for quantification, i.e. from the analysis of the kinetic curves in the SPME fiber. To date, however, the equilibration time for SPME may not be readily used for cases of competitive adsorption between several analytes. It may also be possible to use a sensor to monitor equilibration time, e.g. concentration detection for SPE.

A similar approach may be used for the modeling of competitive adsorption of many analytes. In the simplest case of two analytes with identical diffusion coefficients, a similar approach to that described in this paper could be used, assuming a competitive Langmuir isotherm. Thus, the concentrations of the adsorbed analytes q_1 and q_2, should be described by the following equations

$$q_1 = \frac{k_1 q_s}{k_1 + k_2} \tag{48}$$

and

$$q_2 = \frac{k_2 q_s}{k_1 + k_2} \tag{49}$$

where k_1 and k_2 are the partition coefficients for the competing analytes ''1'' and ''2'', respectively.

The kinetics of desorption may be described as a significant decrease of the equilibrium coefficient k. At such a state, saturation cannot occur, since the critical saturation concentration is very high. This situation is described by Eq. (11) and the boundary conditions in Eq. (12).

It is often assumed that the adsorption equilibrium between the free and adsorbed analytes is established at the analyzed volume-adsorbent layer boundary [15,16]. Then, the diffusion of the free and bound analytes in the adsorbent layer may be examined together without any differences between them. This approach allows simplifying the mathematical problem of the diffusion into the adsorbent layer to the diffusion equation. However, concentration-dependent diffusion in the adsorbent layer needs to be considered. These concentration effects may be caused by the presence of bound analytes [16] in the adsorbent layer and have been observed in SPME extractions.

The modeling approach presented here is relatively simple and uses reasonable assumptions and a simple description of the boundary conditions. Despite its limitations in the proximity of the critical analyte concentration, it has a potential for the introduction of new adsorbent parameters, as well as the introduction of competitive extraction of several analytes. Thus, the models developed and presented in this paper may serve as a ''stepping stone'' for the development of competitive adsorption models in thin layers, e.g. SPME coatings.

The models presented in this paper extend the knowledge related to adsorption processes in SPE/SPME. In particular, these models attempt to describe the kinetics of the adsorption process, and can be used in cases where fast sampling with porous coatings is used [8]. Fast sampling with SPME uses fiber exposure times of less than 10 s, and relies on the diffusion coefficients for quantification. Such sampling is an excellent alternative in field air sampling, fragrance and pheromone applications.

4. Conclusions

The adsorption kinetics of a single analyte into thin adsorptive layer were modeled for several different agitation conditions in the analyzed volume. The resulting models indicated that at some critical value of the oversaturation degree parameter, the saturation of the adsorbent is completed. The critical value of the oversaturation parameter was defined by both the concentration of the analyte in the analyzed volume and the sorbent characteristics. Secondly, it was shown that the adsorption process may be described as the propagation of the saturation adsorption boundary toward the inner boundary of the adsorbent layer. Furthermore, the equilibration time as a function of analyte concentration was estimated for all modeled agitation cases. The equilibration time can be significantly shortened at high degrees of oversaturation and agitation in the analyzed volume.

Acknowledgements

This work was supported in part by the Natural Sciences and Engineering Research Council of Canada and the Russian Foundation for Basic Research (Grant # 98-03-32728). The authors would like to thank Bryn Shurmer and Heather Lord for their help with editing the manuscript.

Appendix A

Eq. (3) and the boundary conditions described by Eqs. (14) and (17) may be not valid at the initial stage of the adsorption when the adsorbent layer is not saturated by the solute. Eq. (3) assumes saturation and the establishment of the equilibrium between free and bound analytes in the adsorbent layer. Thus, for the analyte concentration distribution in the analyzed volume

$$\frac{\partial c_e}{\partial t} = D_e \cdot \frac{\partial^2 c_e}{\partial x^2} \quad \text{at } x \le 0 \tag{A.1}$$

the initial adsorption kinetics should be considered

$$\frac{\partial c_i}{\partial t} = D_i \cdot \frac{\partial^2 c_i}{\partial x^2} - k_- c_i + k_+ q \quad \text{at } x > 0 \tag{A.2}$$

$$\frac{\partial q}{\partial t} = k_- c_i - k_+ q \quad \text{at } x > 0 \tag{A.3}$$

for the free and bound analyte in the adsorption layer, respectively. Coefficients k_+ and k_- are desorption and adsorption rate constants, respectively. At the beginning of the adsorption process, the initial conditions can be described using the following equations

$$c_e(t = 0) = c_0 \quad \text{at } x \le 0 \tag{A.4}$$

$$c_i(t = 0) = 0, \quad q(t = 0) = 0 \quad \text{at } x > 0 \tag{A.5}$$

The boundary conditions at $x = 0$ may be written in the standard form

$$c_i(x = 0) = c_e(x = 0) \tag{A.6}$$

$$D_e \cdot \frac{\partial}{\partial x} c_e(x = 0) = D_i \cdot \frac{\partial}{\partial x} c_i(x = 0) \tag{A.7}$$

Eq. (A.7) corresponds to the conservation of the analyte mass in the analyzed volume and in the adsorption layer. Eqs. (A.1)–(A.3) can be solved using a Laplace transformation

$$c_e(x, s) = A_e \, \mathrm{e}^{\sqrt{(s/D_e)}x} + \frac{c_0}{s} \tag{A.8}$$

$$c_i(x, s) = A_i \, \mathrm{e}^{\sqrt{(1+(k_-/s+k_+))\cdot(s/D_i)}x} \tag{A.9}$$

$$q(x, s) = \frac{k_- c_i(x, s)}{s + k_+} \tag{A.10}$$

where A_e and A_i are the constants, and can be found using the boundary conditions, i.e. Eqs. (A.6) and (A.7), respectively. Finally, the free analyte concentration distribution in the adsorption layer can be estimated using the following equation

$$c_i(x, s) = \frac{c_0}{s} \cdot \frac{\mathrm{e}^{-\sqrt{(1+(k_-/s+k_+))\cdot(s/D_i)}x}}{1 + \sqrt{\left(1 + \dfrac{k_-}{s + k_+}\right) \cdot \dfrac{D_i}{D_e}}} \tag{A.11}$$

The case of a highly efficient adsorbent and fast saturation corresponds to very high values of the transformation parameter s. Assuming a short saturation time, e.g. $s \gg k_+$, k_-, the adsorbent will become saturated earlier than the adsorption equilibrium

$$c_i(x, s) = \frac{c_0}{s \cdot \left(1 + \sqrt{\dfrac{D_i}{D_e}}\right)} \cdot \mathrm{e}^{-\sqrt{(k_-/D_i)}x} \tag{A.12}$$

$$q(x, s) = \frac{k_- c_i(x, s)}{s} \tag{A.13}$$

Eqs. (A.12) and (A.13) describe a steady-state, exponentially decreasing free analyte concentration, and simultaneously increasing spatial profile of the bound analyte concentration

$$q(x, s) = c_0 k_- t \cdot \frac{\mathrm{e}^{-\sqrt{(k_-/D_i)}x}}{\left(1 + \sqrt{\dfrac{D_i}{D_e}}\right)} \tag{A.14}$$

The profile described by Eq. (14a) should increase linearly with time until the analyte concentration reaches the critical saturation value. Since the bound analyte distribution decreases with the increasing distance from the adsorbent surface, the saturation should be first established at the boundary ($x = 0$), when $q(x = 0,\ t) = q_s$ and

$$t_s = \frac{q_s \cdot \left(1 + \sqrt{\frac{D_i}{D_e}}\right)}{c_0 k_-} \quad \text{(A.15)}$$

For large adsorption rate constants, the saturation time t_s should be very small in comparison to both the diffusion equilibration time and the equilibration time for saturation. Thus, immediately after the initiation of the extraction process, a thin saturated layer is established close to the boundary between the adsorption layer and the analyzed volume, with a width of approximately $(D_i/k_-)^{1/2}$. As a result, the time necessary for initial saturation is very short and may be neglected in the analysis of the propagation of the saturation boundary.

References

[1] J. Pawliszyn, Solid Phase Microextraction – Theory and Practice, Wiley, New York, 1997.
[2] J. Pawliszyn (Ed.), Applications of Solid Phase Microextraction, Royal Society of Chemistry, Cambridge, UK, 1999.
[3] I. Stanetzek, U. Giese, R.H. Schuster, G. Wuensch, Am. Ind. Hyg. Assoc. J. 57 (1996) 128.
[4] J. Ai, Anal. Chem. 6 (1997) 1230.
[5] J. Ai, Anal. Chem. 16 (1997) 3260.
[6] J. Ai, Anal. Chem. 22 (1998) 4822.
[7] T. Gorecki, X. Yu, J. Pawliszyn, Analyst 124 (1999) 643.
[8] M. Jia, J. Koziel, J. Pawliszyn, Field Anal. Chem. Technol., in press.
[9] C. Chang, A. Lenhoff, J. Chromatogr. A 827 (1998) 281.
[10] G. Garke, R. Hartmann, N. Papamichael, W. Deckwer, F. Anspach, Sep. Sci. Technol. 34 (1999) 2521.
[11] J. Koziel, M. Jia, A. Khaled, J. Noah, J. Pawliszyn, Anal. Chim. Acta 400 (1999) 153.
[12] G. Guiochon, S.H. Shirazi, A.M. Katti, Fundamentals of Preparative and Nonlinear Chromatography, Academic Press, Boston, 1994.
[13] J. Crank, Mathematics of Diffusion, Clarendon Press, London, UK, 1975.
[14] J. Mattews, R.L. Walker, Mathematical Methods of Physics, W.A. Benjamin, New York, 1965.
[15] N.N. Tunitskij, V.A. Kaminskij, S.F. Timashev, Methods of Physicochemical Kinetics, Khimija, Moscow, 1972, in Russian.
[16] N. Fillipova, J. Colloid Interface Sci. 203 (1998) 464.