Simulation of Near Equilibrium Adsorption Isotherms

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Abstract: Near equilibrium Frumkin adsorption isotherms created by the steady state diffusion at the surface of rotating disk are calculated. The difference between the equilibrium and the near equilibrium isotherms is explained by the time components of the later.

Keywords: diffusion controlled adsorption, Frumkin isotherm, time dependent surface coverage, mathematical modelling.

INTRODUCTION

MANY practical problems, such as the wetting and detergency,[1–3] the purification of wastewaters,[4–8] the stability of foams and emulsions[9–12] and the inhibition of corrosion[13,14] depend on the adsorption of a given substance at a certain interface. The increasing in concentration of adsorbent at the interface as compared with the neighbouring phases depends on the thermodynamics of this phenomenon.[6,9,11,15–17] The adsorption equilibrium isotherms relate surface concentration of adsorbed substance to the bulk concentration of dissolved substance.[3,7,8,18–20] An example is Fowler-Guggenheim, or Frumkin isotherm that is used to describe the adsorption at the solid / liquid interface.[21–23] For a continuous purification of wastewaters the transport of contaminants towards adsorbents is important.[24,25] In the case of diffusion controlled adsorption, the surface concentration of adsorbate depends on time until the equilibrium with the bulk of solution is established.[2,6, 9–11,16,17] In this paper a model of adsorption that is controlled by the diffusion to the rotating disk is developed for Frumkin isotherm. Because of the steady diffusion layer thickness, the flux can be calculated for rather complex surface conditions.

MODEL

It is assumed that a certain surface active substance is dissolved in very low concentration and that it is adsorbing to the surface of a rotating disk under steady state conditions:

$$A \leftrightarrow A_{ads} \tag{1}$$

It is further assumed that the transport within a diffusion layer and the adsorption equilibrium are defined by the following equations:

$$D(c^* - c_{x=0}) / \delta_{ss} = \Gamma_{max} \, d\theta / dt \tag{2}$$

$$\beta c_{x=0} \, e^{a\theta} = \theta / (1 - \theta) \tag{3}$$

Meanings of symbols are reported in Table 1. The differential equation (2) and the isotherm (3) can be transformed into recursive formulae by dividing the time t into M increments:

$$(\theta_m - p)(\theta_m - 1) = z \theta_m e^{-a\theta_m} / M \tag{4}$$

$$p = \theta_{m-1} + z \beta c^* / M \tag{5}$$

$$z = Dt / \beta \Gamma_{max} \delta_{ss} \tag{6}$$

$$\theta_0 = 0 \tag{7}$$

$$1 \le m \le M \tag{8}$$

For the linear isotherm ($\theta \ll 1$) the solution of equations (2) and (3) can be obtained by Laplace transforms:

$$\theta = \beta c * \left[1 - e^{-z} \right] \qquad (9)$$

The corresponding recursive formula is the following one:

$$\theta_m = (\beta c * + \theta_{m-1} M / z) / (1 + M / z) \qquad (10)$$

The solutions of equations (9) and (10) are identical if $M = 1000$.

The left hand side of equation (4) is a parabola that is equal to p if $\theta_m = 0$ and equal to zero if either $\theta_m = p$ or $\theta_m = 1$. The right hand side of this equation is a curve that is equal to zero if $\theta_m = 0$ and exhibits maximum if $\theta_m = a^{-1}$. The solution of equation (4) is the first intersection of these two curves, starting from zero. It can be found by the numerical search. For Langmuir isotherm ($a = 0$) there is an analytical solution:

$$\theta_m = \left(-B - \sqrt{B^2 - 4p} \right) / 2 \qquad (11)$$

$$B = -p - 1 - z / M \qquad (12)$$

It can be used for controlling the numerical procedure.

Table 1. Meanings of symbols.

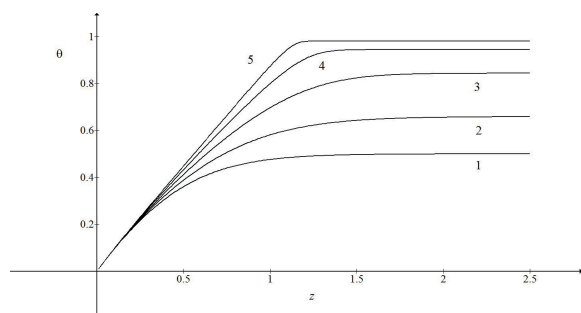|	
a	The coefficient of interactions within the adsorbed layer
$c_{x=0}$	The concentration at the disk surface
$c*$	The bulk concentration of the substance
D	The diffusion coefficient
β	The adsorption constant
Γ_{max}	The maximum surface concentration of the adsorbed substance
δ_{ss}	The thickness of diffusion layer
θ	The surface coverage

Figure 1. Dependence of surface coverage on time; $\beta c* = 1$ and $a = 0$ (1), 1 (2), 2 (3), 3 (4) and 4 (5).

RESULTS AND DISCUSSION

A relative surface concentration of adsorbate ($\theta = \Gamma / \Gamma_{max}$) depends on the dimensionless time variable z (see Eq. 6), the product $\beta c*$ and the interaction parameter a. Some examples are shown in Figure 1. Considering Eq. (9) the linear isotherm is characterized by the initial gradient $(d\theta / dz)_{z \to 0} = \beta c*$ and the equilibrium with the bulk of solution $\theta_{z \to \infty} = \beta c*$. The Langmuir isotherm starts as the linear one and tends to the equilibrium coverage $\theta_{eq} = \beta c* / (1 + \beta c*)$. The apparent adsorption constant of the Frumkin isotherm depends on the coverage: $\beta_{app} = \beta e^{a\theta}$. If $a > 0$ this constant increases with the increasing θ and the equilibrium coverage depends on the interaction parameter. For instance, if $a = 2$ and $\beta c* = 1$, the limiting coverage is $\theta_{eq} = 0.844$, which satisfies the equation: $\theta_{eq} = \beta c* e^{2\theta_{eq}} / (1 + \beta c* e^{2\theta_{eq}})$.

In principle, a diffusion process needs an infinite time to bring the surface coverage into an equilibrium with the bulk of solution. However, this system can approach close to the equilibrium in the definite period that depends on the error of approximation. Figure 2 shows the near equilibrium isotherms that are calculated for the condition: $\theta_{eq}^* = 0.99 \, \theta_{eq}$. For each $\beta c*$ value the surface coverage was calculated as in Figure 1, but not for the same dimensionless time, but until θ was just bigger than θ_{eq}^*. The corresponding near equilibration dimensionless times are shown in Figure 2B.
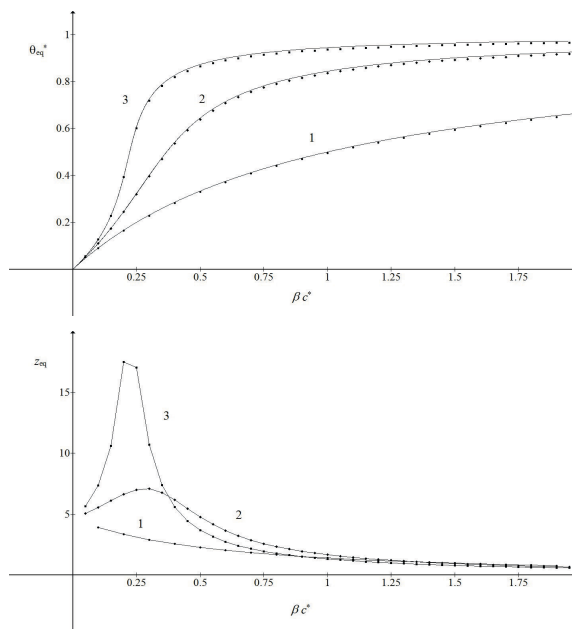

Figure 2. Dependence of near equilibrium surface coverage (symbols) (A) and the corresponding dimensionless times (interconnected symbols) (B) on the product of adsorption constant and the bulk concentration of surface active substance; $a = 0$ (1), 2 (2) and 3 (3). The lines in (A) are equilibrium isotherms.

The lines in Figure 2A are inverse functions of the dependences of βc^* on θ_{eq} that is given by the equilibrium isotherm: $\beta c^* = \theta_{eq}(1 - \theta_{eq})e^{-a\theta_{eq}}$. In the simulation, the equilibrium surface coverage was calculated as the lowest intersection of the straight line $\beta c^*(1 - \theta_{eq})$ and the curve $\theta_{eq}e^{-a\theta_{eq}}$. This procedure is important if $a > 4$.

In the case of Langmuir isotherm the near equilibration dimensionless time decreases uniformly with the increasing βc^* from 3.9 to 0.78. This is in agreement with the theory of linear isotherm: $0.99\beta c^* = \beta c^*(1 - e^{-z_{eq}})$, which results in $z_{eq} = 4.6052$. It seems that the decreasing of z_{eq} with the increasing βc^* is connected to the decreasing gradient: $d\theta_{eq} / d(\beta c^*) = (1 + \beta c^*)^{-2}$. Under the influence of interaction parameter, this gradient is increasing in the range of the smallest βc^* values, which can be seen in Figure 2A. The consequences of these changes are the maxima in the z_{eq} vs. βc^* curves that can be observed in Figure 2B. If $a = 2$, the maximum $z_{eq} = 7.08$ appears for $\beta c^* = 0.3$, and if $a = 3$ the maximum is $z_{eq} = 17.47$ appearing for $\beta c^* = 0.2$. The maxima can be explained by fluxes that are restricted by the bulk concentration of surfactant. If higher surface coverage is to be created by the same flux, then the longer time is needed. This shows that the time component of the near equilibrium isotherm is equally important as the concentration component.

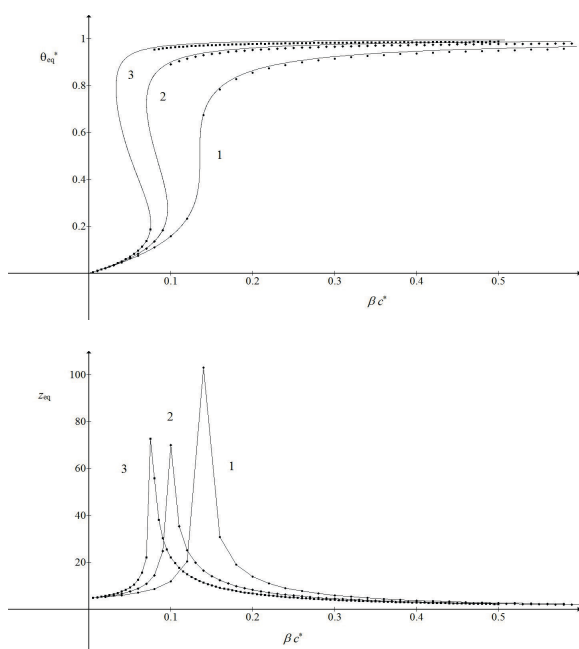Figure 3A shows the near equilibrium and the equilibrium isotherms influenced by strong attractions in

Figure 3. Near equilibrium isotherms (symbols) (A) and the near equilibration dimensionless times (interconnected symbols) (B); $a = 4$ (1), 5 (2) and 6 (3). The lines in (A) are equilibrium isotherms.

the adsorbed layer. The difference between these two types of isotherms originates from the assumption that the surface coverage that is created by the diffusion increases from zero to the lowest value that satisfies the equilibrium isotherm. During this process the concentration of dissolved surfactant at the disk surface increases to the value of the bulk concentration and the diffusional flux is diminished to zero. This is shown in Figures. 4–6. Here is important to observe that the huge jump in surface coverage that is caused by a small increment of βc^* value does not appear suddenly, but it requires a long period of near equilibration, which is shown in Figure 3B. The similarity of time components in this figure suggests that the S shaped equilibrium isotherms are mathematical representation of adsorption – desorption hysteresis because desorption can also be diffusion controlled. However, the maximum near equilibrating dimensionless time depends on the interaction parameter because the later influences the surface concentration of dissolved surfactant, as can be seen in Figures.

The driving force of diffusion controlled adsorption is the gradient of surfactant concentration in the diffusion layer. The surface coverage and the concentration of dissolved substance at the surface are connected by the isotherm (see eqs. 2 and 3). As θ is increasing from zero to the value that satisfies the equilibrium isotherm, the concentration at surface increases from zero to c^*. This occurs during the equilibrating period. Figures 4–6 show the dimensionless surface concentration as a function of dimensionless time.

The curves in Figure 4 correspond to the following points in the curve 3 of Figure 2A: 1, 3, 4, 5, 7, 10 and 20. The highest increasing in θ_{eq}^* appears between βc^* is 0.2 and 0.25, which corresponds to the curves 3 and 4 in Figure 4 and to the maximum of z_{eq} in Figure 2B. Two types of $c_{x=0} / c^*$ vs. z curves can be distinguished in Figure 4. The first one is similar to the exponential curve that is characteristics of linear isotherm: $c_{x=0} / c^* = 1 - e^{-z}$. The curves of this type exhibit very low gradient $d(c_{x=0} / c^*) / dz$ that lasts for long time and maintains low flux because of $c_{x=0} \approx c^*$. The second type is a function of the interaction parameter, as can be seen in Figures. 5 and 6. Also, it explains the maxima in Figures. 2B and 3B. This type exhibits either inflection points or local maxima and minima. It seems that condensations in the adsorbed layer is slowing down the increasing of the concentration of dissolved substance at the surface for a certain period, after which this concentration is increasing faster than in the first type. If $a = 4$ the increasing of surface coverage is the highest between βc^* is 0.12 and 0.14, while for $a = 5$ the jump in θ_{eq}^* happens between βc^* is 0.09 and 0.1. In both Figures. 5 and 6 one can see that this event connects the first and the second type of $c_{x=0} / c^*$ vs. z relationships.
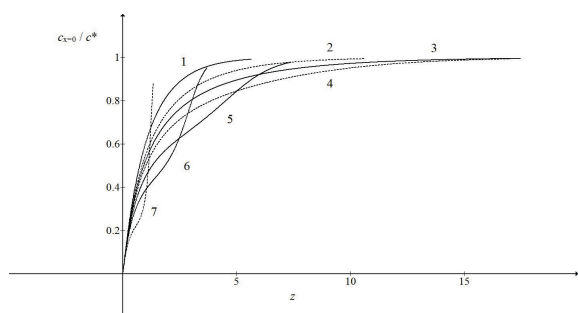
Figure 4. The relationship between the dimensionless concentration of dissolved surface active substance at the disk surface and the dimensionless time; $a = 3$ and $\beta c^* = 0.05$ (1), 0.15 (2), 0.2 (3), 0.25 (4), 0.35 (5), 0.5 (6) and 1 (7).
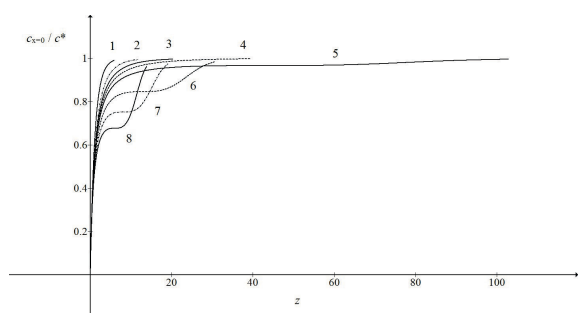

Figure 5. The same as Figure 4; $a = 4$ and $\beta c^* = 0.04$ (1), 0.1 (2), 0.12 (3), 0.13 (4), 0.14 (5), 0.16 (6) 0.18 (7) and 0.2 (8).
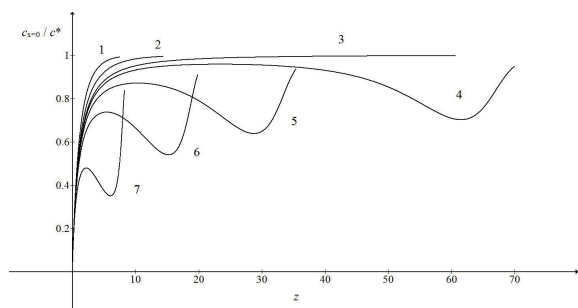

Figure 6. The same as Figure 4; $a = 5$ and $\beta c^* = 0.05$ (1), 0.08 (2), 0.095 (3), 0.1 (4), 0.11 (5), 0.13 (6) and 0.2 (7).

Hence, high surface coverages can be obtained either by the long lasting low flux, or by maintaining the concentration gradient in the diffusion layer high for the shorter period. The later occurs because of the condensation in the adsorbed layer.

Figure 7 shows transient isotherms calculated by Eq. (4) for $a > 4$. They are similar to the curve (5) in Figure 1. If $a = 7$ the equilibrium coverage is $\theta_{eq} = 0.9990831$, which satisfies the equation: $a = [-\ln(\theta_{eq}^{-1} - 1) - \ln(\beta c^*)] / \theta_{eq}$. If $a = 9$ the coverage depends linearly on the dimensionless time: $\theta = 0.982 \, z$. Probably the exponential dependence of β_{app} on θ compensates for the exponential decreasing of θ with time.
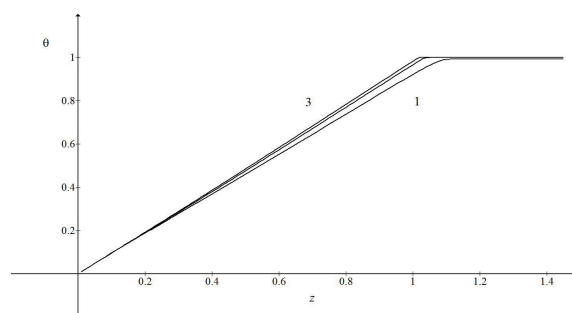

Figure 7. Dependence of surface coverage on time; $\beta c^* = 1$ and $a = 5$ (1), 7 (2) and 9 (3).

CONCLUSIONS

The steady state approximation is useful simplification of the diffusion towards the rotating disk surface. It enables the interpretation of transient isotherms by the comparison with the analytical solution for linear isotherm. The results show that the attraction within the adsorbed layer cannot limit the application of Frumkin isotherm if the adsorption is controlled by the diffusion. As the concentration of dissolved surfactant at the disk surface increases gradually with time, the lowest coverage that satisfies the isotherm is physically meaningful. Its creation consumes the concentration gradient of surfactant in the diffusion layer, which is the driving force of the diffusion controlled adsorption. Hence, no higher surface coverage can be created. The formation of high surface coverage requires either long time of accumulation or maintaining the flux high by keeping the surface concentration low.

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