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Time Dependence of Adsorption at Solid Liquid Interfaces*

Ivica Ružić

Center for Marine Research Zagreb, »Ruđer Bošković« Institute, Zagreb, Croatia, Yugoslavia

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In this paper the time dependence of adsorption at solid-liquid interface is discussed for both the mass-transport and intrinsic kinetic control of the adsorption process. It has been shown that the time dependence of adsorption of the mass-transport control of the adsorption process is mostly dependent on the strength of adsorption (natural diffusion) and sometimes on the mass-transport coefficient (dispersion coefficient in the case of eddies), which appear in natural environments). For the intrinsic kinetic control of adsorption several rate laws, are reviewed. Methods for the interpretation of adsorption experiments available in the literature are discussed. The possibility of distinguishing the mass-transport and kinetic control is mentioned. Simple models of a two-step adsorption process are described assuming the first step to be a very fast attachment of adsorbate from the homogeneous phase to the interface. It is concluded that for a correct interpretation of adsorption experiments the impression that adsorption is under equilibrium conditions should always be supported by the right shape of the adsorption isotherm. Otherwise additional experiments should be performed in a wider range of adsorption times.

INTRODUCTION

Adsorption kinetics has been long recognized as a subject of special importance from the academic, as well as from practical points of view. Adsorption kinetics certainly plays an important role, for example, in catalysis[1], detergency[2], drug administration[3], fate of pollutants in the environment[4], flotation[5,6], and the uptake of nutrients by biota. Although most of the research on adsorption processes at different types of interfaces has been concerned with adsorption equilibrium, a substantial number of results on kinetics of adsorption has been accumulated so far[7–27].

There are some difficulties in studying adsorption kinetics, as mentioned in literature[12,14]. The first one is the paucity of theories and models available for comparison with experiments. Then there are also experimental difficulties encountered in the measurements of the rate of adsorption. For example Benson and Ellis[27] noted that the time dependence of adsorption of water

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on lyophilised proteins appeared due to the time variation of temperature caused by the heat evolved on adsorption on subsecond cooling of the sample. Mycels[28] reported time dependent adsorption as an artifcat due to the slow adsorption of highly surface-active impurities.

Usually it is assumed that the relaxation time for the first attachment of the adsorbate molecules on the interface is of the order of magnitude of the time necessary for the formation of the interface itself[29], between 10 and 100 μ sec. Therefore, the first attachment of the adsorbate molecules to the interface very often occurs under steady state conditions. Assuming the adsorbtion kinetics at the interface to be a first order process which is coupled with mass transport of the adsorbate molecules from the bulk of homogeneous phase to the interface, such a steady state can be described using the following relation:

$$k_A C_o \approx k_T (C^* - C_o) \tag{1}$$

where C_o and C^* are the volume concentrations of the adsorbate near the interface and in the bulk of homogeneous phase, while k_A and k_T are the rate constants of the adsorption process at the interface and the mass transport rate constant, respectively. The rate of adsorption at the interface $k_A C_o$ can then be described by elimination C_o from eqn. (1) in the following way:

$$k_A C_o \approx k_A k_T C^*/(k_A + k_T) \tag{2}$$

The overall rate constant is $k = k_A k_T/(k_A + k_T)$ or after some rearrangement:

$$1/k = 1/k_A + 1/k_T \tag{3}$$

Since the first attachment of the adsorbate to the interface is supposed to be very fast, very often $k_A \gg k_T$ should be true and consequently the overall rate will be often controlled by mass transport as a rate determining step $k \approx k_T$.[30–48] The same reasoning is valid for any heterogeneous process at the interface with the reactant dissolved in the homogeneous phase. However, the first attachment of the adsorbate to the interface could be followed by a whole series of different heterogeneous processes of very different relaxation times. Some of these processes may under certain conditions be slower than the mass transoprt itself. In such cases the equilibrium between the bulk of homogeneous phase and the volume concentration near the interface can be established at the time scales of the relaxation time of these secondary heterogeneous processes. Then, the time dependence of adsorption can be controlled by the so called intrinsic adsorption kinetics. Such secondary heterogeneous processes can be: reorientation of adsorbed molecules, surface diffusion, surface complexation, formation of new phases through an interaction of adsorbed molecules, degradation of larger molecules producing adsorbates of lower molecular weight and different adsorption characteristcs etc.[40–52]. In addition, a whole series of homogeneous reactions can take place in some cases. The kinetics of these homogeneous reactions can be induced within the mass transport layer by heterogeneous processes at the interface.

In this paper different models for time dependence of adsorption at solid liquid interfaces reported so far in literature will be discussed. Different methods for the determination of adsorption parameters will be also discussed.

STATIONARY MASS TRANSPORT

Let us assume that a very fast adsorption process is taking place on a quiet interface with a certain radius of surface curvature r_o. The adsorbate is present in the bulk of the homogeneous phase in concentration C^* and the diffusion coefficient of the adsorbate is D. The mass transport can be described by the following equation:

$$\mathrm{d}C/\mathrm{d}t = (D/q^2)\,\mathrm{d}\,(q^2\mathrm{d}C/\mathrm{d}r)/\mathrm{d}r \tag{4}$$

where r is the space coordinate, t is time and q is the geometry parameter ($q = 0$ for planar, $q = 1$ cylindrical and $q = 2$ spherical interface). Eqn. (4) is subjected to the following initial, limiting and boundary conditions:

$$t = 0, \quad r \geqslant r_o, \quad C = C^*$$

$$t > 0, \quad r \rightarrow \infty, \quad c \rightarrow C^*$$

$$r = r_o, \quad D\,(\mathrm{d}C/\mathrm{d}r) = \mathrm{d}\Gamma/\mathrm{d}t$$

where Γ is the surface concentration of the adsorbed molecules at the interface. Consequently, the rate of adsorption $\mathrm{d}\Gamma/dt$ represents the surface boundary condition to the mass transport eqn. (4). By solving eqn. (4) the expresion for concentration profile near the interface can be obtained:

$$C = C^*\,(1 - I) \tag{5}$$

where

$$I = (\sqrt{D}/C^*) \int (\mathrm{d}C/\mathrm{d}r)_{\mathrm{r}=\mathrm{r_o}}\; \xi\,(r,r_o,t - \tau)\,d\tau = \frac{1}{C^*\sqrt{\mathrm{D}}} \int \frac{\mathrm{d}\Gamma}{\mathrm{d}\tau}\,\xi\,(r,r_o,t - \tau)\,d\tau$$

and the function ξ depends on the geometry of the interface. Stationary mass transport is characterized by time independent concentration of adsorbate near the interface:

$$C_{\mathrm{r}=\mathrm{r_o}} = C^*\,(1 - I_o) \tag{6}$$

where

$$I_o = (\sqrt{D}/C^*) \int (\mathrm{d}C/\mathrm{d}r)_{\mathrm{r}=\mathrm{r_o}}\; \xi_o\,(r_o,t - \tau)\,\mathrm{d}\tau = \frac{1}{C^*\sqrt{D}} \int \frac{\mathrm{d}\Gamma}{\mathrm{d}\tau}\,\xi_o\,(r_o,t - \tau)\,d\tau$$

Applying Laplace transformations to eqn. (6) the following result can be obtained if $C_{\mathrm{r}=\mathrm{r_o}}$ is assumed to be time independent (steady state):

$$L\,\{(\sqrt{D}/C^*)\,(\mathrm{d}C/\mathrm{d}r_{\mathrm{r}=\mathrm{r_o}}\,\} = I_o/sL\,\{\xi_o\}$$

where 1/s is the Laplace transform of t. If the Laplace transformation of the function ξ_o is available, then the rate of adsorption can be obtained in the following way:

$$D\,(\mathrm{d}C/\mathrm{d}r)_{\mathrm{r}=\mathrm{r_o}} = \mathrm{d}\Gamma/\mathrm{d}t = I_o\,\sqrt{D}\,C^* L^{-1}\,[1/sL\,\{\xi_o\}] \tag{7}$$

Analytical expression for the ξ_o function is available only for planar ($q = 0$ or $r_o \rightarrow \infty$) and spherical ($q = 2$) interfaces:

$$\mathrm{d}\Gamma/\mathrm{d}t = I_o\,\sqrt{D}\,C^*\,(1/\sqrt{\pi t} + \sqrt{D}/r_o)$$

wherefrom

$$\Gamma = I_o\,(2\sqrt{Dt/\pi} - Dt/r_o) \tag{8}$$

Here $I_o = 1 - C_o/C^*$, is a constant with respect to time. From eqn. (8) describing the surface concentration one can derive an expression for the surface coverage $\Theta = \Gamma/\Gamma_m$ (Γ_m being the surface concentration of the complete monolayer) in terms of two dimensionless parameters $G_m = \Gamma_m/C^*\sqrt{Dt}$ and $S = \sqrt{Dt}/r_o$ (known as sphericity):

$$\Theta = I_o\,(2/\sqrt{\pi} - S)/G_m \tag{9}$$

As it has been shown by numerical calculations[32] the time necessary to attain the equilibrium between the bulk of the homogeneous phase and the volume near the interface can be obtained from the following condition:

$$G_m < 0.1 \text{ or } t > 100\,\Gamma_m^2/(C^{*2}D) \text{ if } S \ll 1$$

In cases where S is comparable to unity the mass transport is more efficient and the adsorption equilibrium can be attained faster. Usually $\Gamma_m/\sqrt{D}$ is not very different for different adsorbates and its value is between 10^{-8} to 10^{-7} mol sec$^{1/2}$/cm^3. Therefore, the condition necessary to attain the adsorption equilibrium can be also written in the following way:

$$C^*\sqrt{t} > 10^{-7} \text{ to } 10^{-6} \text{ mol sec}^{1/2}/\text{cm}^3$$

In Table I the times necessary for attaining the adsorption equilibrium are presented for different bulk concentrations of the adsorbate according to the above mentioned condition. It is obvious that at bulk concentrations of about 0.1 mol/l the relaxation time for the first attachment of the adsorbate to the interface is of the order of time necessary to attain the equilibrium with the bulk of the homogeneous phase. Therefore, this is a case of coupling between the time scales of the mass transport and the first attachment of the adsorbate to the interface.

However, in the case of lower ionic strengths the times necessary to attain the adsorption equilibrium by natural diffusion could be significantly higher than those suggested in Table I. In such conditions the potential profile near the interface (ψ) represents an energy barrier to diffusion, as suggested by Kimizuka et al. (54—56). In the case of sodium dodecyl sulphate, tridecyl sulphate and hexadecyl sulfate these authors reported the energy barrier in the range between 0.5 to 2.5 kcal/mol at 28 °C. As a consequence, the G_m values

TABLE I

Conditions Necessary for Attaining the Adsorption Equilibrium with the Bulk of the Homogeneous Phase by Natural Diffusion for S ≪ 1 *and High Ionic Strengths*

C^* in mol/l	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}
t	1—100 μsec	10—1000 msec	1—100 min	10—1000 days*	300—3000 years*

* in reality influenced by natural convection and the adsorption equilibrium is then attained foster.

decrease between one and two orders of magnitude and for the same factor the time necessary to attain the adsorption equilibrium should be increased. For times of adsorption longer than several minutes, in addition to natural diffusion, one should also take into account the convective contributions to mass transport. Therefore, for bulk concentrations smaller than 10^{-6} mol/l the time necessary to attain the adsorption equilibrium will be significantly shorter than those predicted in Table I. In a natural environment, mass transport is controlled by different scales of eddies[57] and therefore the establishment of adsorption equilibrium will be more efficient, as shown in Table II.

TABLE II

The Longest Times Necessary to Attain Adsorption Equilibrium in Natural Aquatic Systems

Aquatic systems	Concentration levels in mol/l		
	10^{-3}	10^{-6}	10^{-9}
Pore water in sediments	100 msec	1 day	3000 years
Ground water of alluvial aquifers	1 msec	15 min	30 years
Surface waters	a	10 msec	10 sec

Symbol »a« refers to the intrinsic kinetics of the first attachment to the interface.

INTRINSIC ADSORPTION KINETICS

From the steady state condition for adsorption equilibrium one can conclude that mass transport will control time dependence of adsorption for strongly adsorbable substances. In tis case measurable surface coverages will be attained at concentrations which are of the order of magnitude of $C^* \approx 1/K$ (K being the adsorption equilibrium constant). It has been suggested (50) that the condition to attain the adsorption equilibrium with the bulk of homogeneous phase can be also described through a dimensionless quantity which contains K instead of C^*:

$$t > 100\, \Gamma_m^2 K^2/D$$

However, the time dependence of adsorption process at time scales of minutes, hours and even days have been observed also for adsorbates undergoing relatively weak adsorption (for example in cases of some aliphatic alcohols and fatty acids as well as macromolecules). Measurable surface coverages can be obtained in such cases only at relatively high bulk concentrations of adsorbates. Under such conditions, mass transport cannot explain the time dependence of adsorption, even when only natural diffusion can take place. Therefore, for such cases there must be an energy of barrier to adsorption process responsible for time dependence of the adsorption process. If the first attachment to the interface is very fast, then such intrinsic adsorption kinetics should be a result of some kind of secondary interaction (reaction) with the surface.

The first experiments of the intrinsic adsorption kinetics reported in the first half of this century suggest the following conclusions[58-62]:

i) The rate of adsorption in always proportional to the concentration of the adsorbate in the bulk of the homogeneous phase: $v_a \propto k_a C$.
ii) Sometimes the adsorption rate is also proportional to the free surface and desorption rate to the surface coverage: $v_a \propto (1 - \Theta)$ and $v_d \propto \Theta$.
iii) Few examples are known of the rate of adsorption proportional to the higher power of the free surface: $v_a \propto (1 - \Theta)^2$ or $v_a \propto (1 - \Theta)^3$.

On the basis of this knowledge the simplest first order kinetic model for the adsorption process can be obtained:

$$d\Theta/dt = k_a C - k_d \Theta \tag{10}$$

This classical rate equation has the known analytical solution:

$$\Theta = (k_a C/k_d)\,(1 - e^{-k_d t}) = KC\,(1 - e^{-k_d t}) \tag{11}$$

The adsorption equilibrium according to this model $\Theta = KC$ corresponds to the so called Henry (or ideal) adsorption isotherm. Combining this adsorption isotherm with the thermodynamic Gibbs relation $\partial\gamma/\partial \ln C = - RT\Gamma$ (where γ is the surface tension) one can easily derive the ideal equation of state for adsorption: $\pi = RT\Gamma$ (which is equivalent of the equation of state for an ideal gas (here π is the surface pressure $\gamma_o - \gamma$, and γ_o is the surface tension for $\Gamma = 0$).[11,63]

According to Langmuir hypothesis on the nature of the adsorbed layer, the above simplest rate law can be extended to the following more general form[58,59]:

$$d\Theta/dt = k_a C\,(1 - \Theta - k_d \Theta \tag{12}$$

This Langmuirian rate law has the analytical pseudo-first order solution (for cases where the bulk concentration of adsorbate is not significantly affected by the adsorption processes):

$$\Theta = (k_a C/\varepsilon)\,(1 - e^{\varepsilon t}),\ \text{where } \varepsilon = k_a C + k_d \tag{13}$$

The adsorption equilibrium according to this model $\Theta = KC/(1 + KC)$ corresponds to the well known Langmuirian adsorption isotherm. This model has been widely used for the interpretation of experimental results by many authors.[13,64-68] On the basis of the Langmuir type of adsorption isotherm a special method has been developed for the determination of the adsorption equilibrium constant. According to this method, the plotting of the inverse values of Θ vs C should produce a straight line of slope equal to $1/K$ in the case of adsorption equilibrium[7]:

$$1/\Theta = 1 + 1/KC$$

This method has been widely used in literature. However, it has been shown recently[50] that this method is not selective enough for distinguishing the adsorption equilibrium from the adsorption kinetics. Therefore, in the case of the very slow time dependence of adsorption, the adsorption equilibrium can be significantly underestimated using this method. Therefore, another method has been proposed[50], based on plotting $\Theta/(1-\Theta)$ vs. C in a log-log diagram. In the case of adsorption equilibrium this plot has the form of a straight line of unit slope:

$$\log[\Theta/(1-\Theta)] = \log C + \log K$$

The adsorption equilibrium constant can be determined from the intersection of this straight line with the abscissa. The form of this plot deviates from a straight line in the case of time dependence of adsorption as shown in Figure 1. In some cases both the equilibrium constant and the rate constant can be determined from this plot[50].

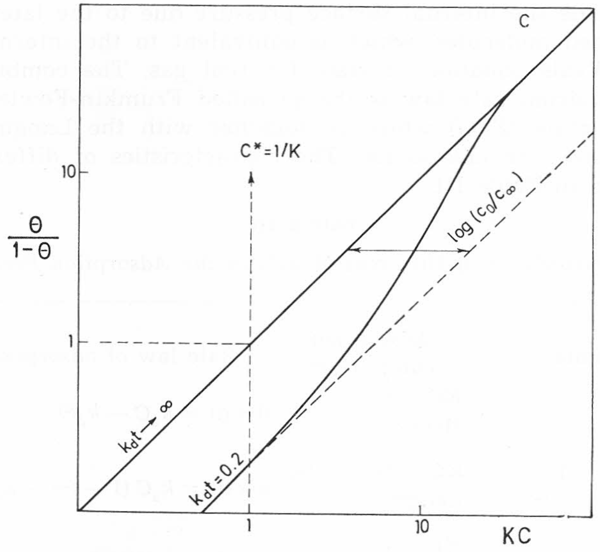

Figure 1. Plot of $\Theta/(1-\Theta)$ vs. C (KC for theoretical predictions) in a log-log diagram for the case of Langmuirian adsorption, and two different values for k_dt parameter. Equilibrium condition (which corresponds to $k_dt \rightarrow \infty$) has the form of a straight line which is at the same time an asymptote to the plot at higher surface coverages.

As mentioned above, the rate of adsorption is not always proportional to the free surface. Roginsky and Zeldovich were able to fit some of the experimental results using the exponential type of the adsorption rate law:

$$d\Theta/dt = K_aC\, e^{-a\Theta} \tag{14}$$

known as the Elovich eqn.[69-72]. This rate law has also an analytical solution:

$$\Theta = (1/a) \quad \ln(1 + aK_aCt) \tag{15}$$

Delahay and Mohilner[10,23,63] extended this kind of rate law by including an additional term for desorption rate:

$$d\Theta/dt = k_aC\, e^{-a_1\Theta} - k_d\, e^{a_2\Theta} \tag{16}$$

No analytical solution for this rate law is available and, therefore, numerical methods should be used to obtain the solution. The corresponding adsorption equilibrium $KC = e^{b\Theta}$ (where $b = a_1 + a_2$) is known as the Temkin adsorption isotherm. A more general model of adsorption kinetics can be described by the following rate equation:

$$\mathrm{d}\Theta/\mathrm{dt} = k_{\mathrm{a}}C\, e^{a^{-}_{1}\Theta} - k_{\mathrm{d}}\Theta\, e^{a_2\Theta} \tag{17}$$

The corresponding adsorption equilibrium $KC = \Theta e^{b\Theta}$ represents the so called virial adsorption isotherm[11,63]. The meaning of coefficient b can be deduced from the corresponding equation of state for adsorption:

$$\pi + \pi_{\mathrm{i}} = RT \quad \text{where} \quad \pi_{\mathrm{i}} = -RTb\, \Gamma^2/2\, \Gamma_{\mathrm{m}}$$

Here π_{i} represents the internal surface pressure due to the lateral interaction between adsorbed molecules, which is equivalent to the internal pressure in the Van der Waals equation of state for real gas. The combination of this and the Langmuirian rate law is the so called Frumkin-Fowler-Guggenheim model of adsorption (FFG) which is, together with the Langmuirian model, most widely used rate law so far. The characteristics of different rate laws are summarized in Table III.

TABLE III

Characteristics of Different Models of the Adsorption Process

Eqn. of state	Adsorption equilibrium	Rate law of adsorption	Ref.
$\pi = RT\, \Gamma_{\mathrm{m}}\Theta$	$KC = \Theta$ Henry	$\mathrm{d}\Theta/\mathrm{dt} = k_{\mathrm{a}}C - k_{\mathrm{d}}\Theta$	24, 25
$\pi = RT\, \Gamma_{\mathrm{m}} \cdot \ln\left(\frac{1}{1-\Theta}\right)$	$KC = \Theta/(1-\Theta)$ Langmuir	$\mathrm{d}\Theta/\mathrm{dt} = k_{\mathrm{a}}C\,(1-\Theta) - k_{\mathrm{d}}\Theta$	26, 58, 59
$\pi = RT\, \Gamma_{\mathrm{m}}\, \mathrm{b}\Theta^2/2$	$KC = e^{\mathrm{b}\Theta}$ Temkin	$\mathrm{d}\Theta/\mathrm{dt} = k_{\mathrm{a}}C^{-\mathrm{a}_1\Theta} - k_{\mathrm{d}}e^{\mathrm{a}_2\Theta}$	10, 19, 22
$\pi = RT\, \Gamma_{\mathrm{m}} \cdot (\Theta + \mathrm{b}\Theta^2/2)$	$KC = \Theta e^{\mathrm{b}\Theta}$ Virial	$\mathrm{d}\Theta/\mathrm{dt} = k_{\mathrm{a}}Ce^{-\mathrm{a}_1\Theta} - k_{\mathrm{d}}\Theta e^{\mathrm{a}_2\Theta}$	
$\pi\, RT\, \Gamma_{\mathrm{m}} \cdot [\ln\left(\frac{1}{1-\Theta}\right) +$ $+ \mathrm{b}\Theta^2/2]$	$KC = \Theta e^{\mathrm{b}\Theta}/$ $/(1-\Theta)$ *FFG*	$\mathrm{d}\Theta/\mathrm{dt} = k_{\mathrm{a}}C\,(1-\Theta)\, e^{-\mathrm{a}_1\Theta} -$ $- k_{\mathrm{d}}\Theta e^{\mathrm{a}_2\Theta}$	51, 73, 84

In the next section of this paper the FFG type of adsorption model will be discussed in more.

FFG AND SIMILAR MODELS OF ADSORPTION

Combining the Langmuirian and virial models of adsorption, i. e. including the internal surface pressure into the Langmuirian type of equation of state, one can derive the FFG type of adsorption isotherm $KC = \Theta e^{b\Theta}/(1-\Theta)$. The corresponding rate law can be written in the following way[50,51,73]:

$$\mathrm{d}\Theta/\mathrm{dt} = k_{\mathrm{a}}C\,(1-\Theta)\, e^{-\mathrm{a}_1\Theta} - k_{\mathrm{d}}\Theta e^{a_2\Theta} \tag{18}$$

This type of adsorption rate law has been used extensively for the interpretation of adsorption of electroactive species at the electrode-electrolyte interface[10,20,24]:

$$i = nFA\,k_s\,[C_o\,(1 - \Theta)\,e^{-a_1\Theta - \alpha\xi} - \Theta e^{a_2\Theta + (1-\alpha)\xi}] \tag{19}$$

where i is the electric current, α is the electrochemical transfer coefficient, A is the electrode surface, $\xi = nF\,(E - E_o)/RT$ (n is the number of electrons involved in electrode reaction, F is the Faraday constant, E the electrode potential), and E_o, k_s are the standard potential and standard rate constant respectively. The FFG type of adsorption rate law has also been successfully used for the interpretation of adsorption of electroinactive species.[73] The FFG type of rate law can be rewritten in terms of parameters of adsorption equilibrium in the following way:

$$\mathrm{d}\Theta/\mathrm{d}t = k_d\,[KC\,(1 - \Theta)\,e^{-\lambda b\Theta} - \Theta e^{(1-\lambda)b\Theta}] \tag{20}$$

where λ in an additional kinetic parameters. The rate law (20) cannot be solved analytically and some numerical methods, such as Runge-Kuta, should be used to obtain theoretical predictions. Comparison of experimental results within the FFG type of rate alw requires determination of two additional parameters to those of the Langmuirian type of rate law. These are the FFG type of inreaction coefficient b and the corresponding kinetic parameter λ. For the case of adsorption equilibrium Damaskin and Dyatkina[74] proposed the use of the plot of log $C\,(1 - \Theta)/\Theta C_{\Theta=1/2}$ vs. Θ. In such a case, this semilogarithmetic plot should have the form of a straight line of the slope equal to b log e. However, in the case of time dependence of adsorption, a whole range of surface coverages are not in adsorption equilibrium and the use of this kind of plot can be a significant source of errors. It has been also suggested to use a similar semilogarithmic plot of log $\Theta/C\,(1 - \Theta)$ vs. Θ, which can be described for the FFG type of adsorption by the following equation[50,51]:

$$\log\,[\Theta/C\,(1 - \Theta)] = \log K - b\log e$$

In the absence of time dependence of adsorption, on the basis of this plot one can obtain the values of both the adsorption equilibrium constant K and the FFG type of interaction coefficient b. If the time dependence of adsorption cannot be neglected, all adsorption parameters cannot be easily obtained from the experimental results. However, it has been shown that this plot is not very sensitive to the value of λ parameter and that it can be assumed that $\lambda \approx 0.5$, i. e. $a_2 \approx - a_1 \approx b/2$ is a reasonable approximation[50]. The rest of adsorption parameters, K, k_dt and b can be extracted from the experiments by comparison with theoretical plots for different times of adsorption. For the same purpose one can use the same log-log plot as for the Langmuirian type of adsorption ($\Theta/(1 - \Theta)$ vs. C). The separation between the asymptotes at low and high coverages for this plot will depend on the FFG type of interaction coefficient, as shown in Figure 2. Adsorption parameters can be determined from this plot by comparing the separation of these asymptotes (C_o/C_∞) for different times of adsorption, as shown in Figure 3. In the case of high values for the FFG interaction coefficient b the separation between asymptotes can be

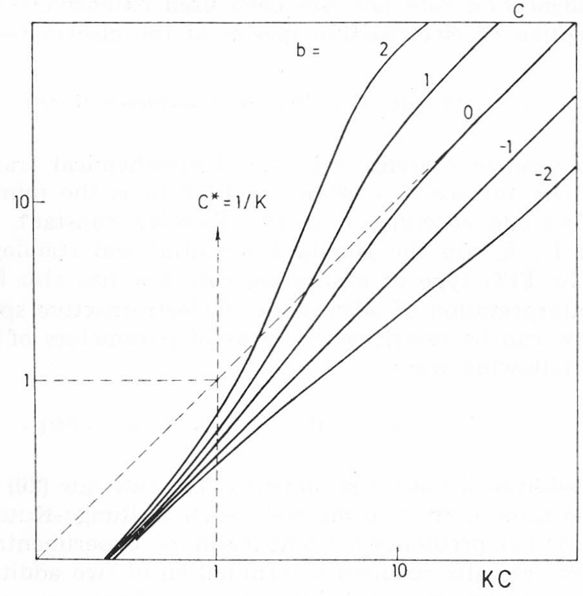

Figure 2. Plot of $\Theta/(1-\Theta)$ vs. C (KC for theoretical predictions) in a log-log diagram for the case of the FFG type of adsorption, and different values for the FFG interaction coefficient »b«. Other parameters are $k_d t = 0.5$ and $\lambda = 0.5$.

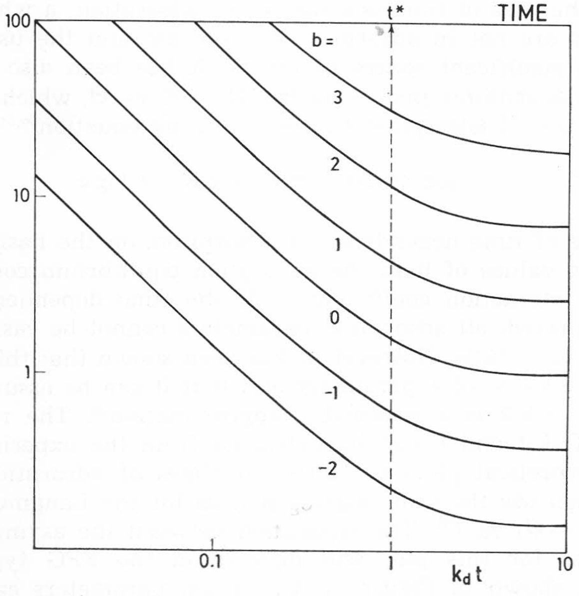

Figure 3. Plot of separation between asymptotes at low (C_0) and high (C_∞) surface coverages for the FFG type of adsorption and different values of the FFG interaction coefficient »b«. Adsorption parameters are the same as in Figure 2.

arbitrary constant. In this way one can increase the accuracy of determination of the separation between the assymptotes[50].

The determination of adsorption parameters and their reliability in predicting the time dependence of adsorption depends strongly on the type of adsorption isotherm chosen for the interpretation of experimental results. Therefore, it would be useful to develop reliable diagnostic criteria for the selection of an appropriate type of adsorption isotherm. For this purpose another plot has been proposed where $\log \Theta/C$ is plotted vs. $\log(1 - \Theta)$[50]:

$$\log(\Theta/C) = \log K + \log(1 - \Theta) - b\,\Theta \log e$$

In the case of the Langmuirian type of adsorption this plot should have the form of a straight line, of unit slope while in the case of the FFG type of adsorption a straight line can be obtained only at higher coverages. For very negative values of the interaction coefficient b (attraction of adsorbed molecules) this plot is characterized by distrinct maximum at moderate surface coverages, as shown in Figure 4. This plot is also very selective in distinguishing the time dependence of adsorption from the adsorption equilibrium. The intersection with the ordinata at zero surface coverage gives the value for the adsorption equilibrium constant. From the comparison of experiments and theoretical plots for different times of adsorption one can extract the value for the adsorption rate constant as well.

Long ago Sweringen and Dickinson[68] introduced the concept of the shift from the adsorption equilibrium $\Theta = (C^{0} - C)/(C^{0} - C^{\infty})$ where C^{0} and C^{∞} represent adsorbate concentrations at the beginning of the experiment and

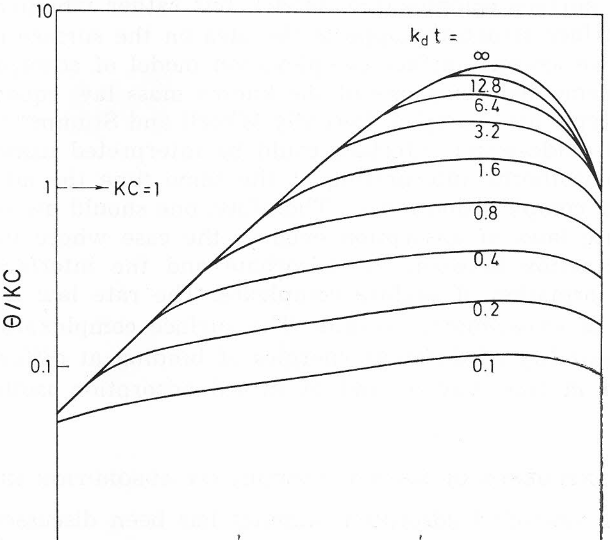

Figure 4. Theoretical plots of Θ/KC vs. $1 - \Theta$ in a log-log diagram for the FFG type of adsorption and different $k_{d}t$ values. Other parameters are $b = 4$ and $\lambda = 0.5$.

in the equilibrium, respectively. Using this concept Fava and Eyring proposed the following rate equation[21]:

$$\mathrm{d}\Theta/\mathrm{d}t = 2k\,(1 - \Theta)\,\sinh\,[b\,(1 - \Theta] \tag{21}$$

where they assumed the adsorption and desorption rate constants to be equal. This unnecessary assumption has been avoided by Lindstrom and Haque who proposed the following modified version of the adsorption rate law[22]:

$$\mathrm{d}\Theta/\mathrm{d}t = k_\mathrm{a}\,(1 - \Theta)\,(1 - \Theta/2)\,e^{-\mathrm{b}\Theta} - k_\mathrm{d}\,[(1 - \Theta/2)\,e^{\mathrm{b}(2-\Theta)} - \Theta^2\,e^{\mathrm{b}\Theta}/2] \tag{22}$$

These rate laws are based on similar principles to the rate law which corresponds to the FFG adsorption isotherm. However, in rate equations (21) and (22) the information about the adsorption equilibrium is lost and, therefore, they are not convenient for the interpretation of experimental results even if a reasonably good fitting can be attained.

Theory of adsorption of metal ions at hydrous oxide surfaces is based on the model of adsorption involving surface complexation[75-79]. However, this model of adsorption cannot be conceptually directly connected with any particular type of adsorption isotherm. In fact, it can equally well accommodate Langmuirian, and the FFG type of behaviour. In comparison with the surface complexation model the adsorption isotherm represents a formal mass law equation (which can be mathematically similar for adsorption and for any homogeneous chemical reaction, such as complex formation in solution). The surface complexation model refers to the nature of the binding of adsorbed molecules at the interface and not the type of mass law equation, it would, therefore, be incorrect to argue whether one should use Langmuirian, FFG or the so called surface complexation model, but rather whether the energy or binding or surface structure supports the idea on the surface complexation or not. Even if we assume surface complexation model of adsorption, this model could be implemented using one of the known mass law equations (Langmuirian or FFG type, for example). Recently Wherli and Stumm[80,81] suggested that adsorption of oxide-water interface could be interpreted using the FFG type of adsorption isotherm, interpreting at the same time the adsorption process by the surface complexation model. Therefore, one should use one of the above mentioned rate laws of adsorption even in the case where there is evidence that the interaction between the adsorbate and the interface is manifested through the formation of surface complexes. The rate law should be chosen on the basis of experimental results. The surface complexation model introduces the possibility of different energies of binding at different sites at the interface and in this way a kind of mixed adsorption isotherm[79] could be obtained.

THE INFLUENCE OF MASS TRANSPORT ON ADSORPTION KINETICS

Diffusion controlled adsorption kinetics has been discussed by Ward and Torday.[17] They presented an integral equation for planar and quiet interface similar to eqn. (6): Generally, one can write:

$$\Gamma = C^{*}\,\sqrt{D} \int I_\mathrm{o}\,(t - \tau) \cdot L^{-1}\,[1/s\,\{\xi_\mathrm{o}\}]\,\mathrm{d}\tau \tag{23}$$

and in the case of the planar and spherical interface:

$$\Gamma = C^* \sqrt{D} \int I_o (t - \tau) \left(\frac{1}{\sqrt{\pi\tau}} + \frac{\sqrt{D}}{r_o} \right) d\tau = C^* 2 \frac{Dt}{\pi} \left(1 + \frac{\sqrt{\pi Dt}}{2r_o} \right) - \sqrt{D} \int C_{o,\mathrm{I}=\mathrm{I}}$$

$$(t - \tau) \left(\frac{1}{\sqrt{\pi\tau}} + \frac{\sqrt{D}}{r_o} \right) d\tau \qquad (24)$$

This integral eqn. can be combined with a given adsorption isotherm and in this way the solution for the pure mass transport control of adsorption can be obtained. For Henry (ideal) adsorption isotherm such a solution should read:

$$\Gamma = C^* \sqrt{D} \, [K \Gamma_m / \sqrt{D} + A \, e^{a^2 t} \operatorname{erfc} a \sqrt{t} + B \, e^{b^2 t} \operatorname{erfc} b \sqrt{t}]$$

where

$$A = (1 - \sqrt{D}/ar_o)/(b - a)$$

$$B = (1 - \sqrt{D}/br_o)/(a - b)$$

$$a + b = \sqrt{D}/K\Gamma_m$$

$$a \cdot b = D/K \, \Gamma_m r_o$$

For planar interface this solution reduces to the expression reported earlier by Delahay and Trahtenberg[32]:

$$\Gamma = KC^* \Gamma_m \, [1 - e^{Dt/K^2 \Gamma_m^2} \operatorname{erfc} \sqrt{Dt}/K\Gamma_m$$

Analogous numerical solutions have been obtained for the Langmuirian[35-37], as well as the FFG type of isotherms[73].

Combining the eqn. (24) and a rate law for adsorption one can derive a solution for cases of coupling between the intrinsic adsorption kinetics and mass transport. In the case of the planar interface and linear rate law of adsorption (eqn. 10) the following solution can be obtained[24,25]:

$$\Gamma = K\Gamma_m C^* \left(1 + \frac{b}{a - b} \, e^{a^2 t} \operatorname{erfc} a \sqrt{t} + \frac{a}{b - a} \, e^{b^2 t} \operatorname{erfc} b \sqrt{t}\right)$$

For other rate laws only numerical solutions can be used. Recently, such a numerical solution for the FFG type of adsorption has been used for the interpretation of adsorption kinetics of Triton-X-100 at the mercury-sodium chloride interface (hanging mercury electrode with nearly spherical geometry)[73].

In Figure 5 log-log plots of $\Theta (1 - \Theta)$ vs. C are compared for cases of pure diffusion and intrinsic kinetic control of the Langmuirian type of adsorption. Obviously, the shapes of there two plots are different at higher coverages and shorter time of adsorption. Therefore, it is possible to distinguish these two cases from the experimental results[50,73].

Time dependence of adsorption of sodium dodecyl sulfate at the mercury-sodium chloride interface has not been successfully interpreted with the same model. Discrepancies have been observed between the theory and experiment at longer times of adsorption[83]. Experimental results on the time

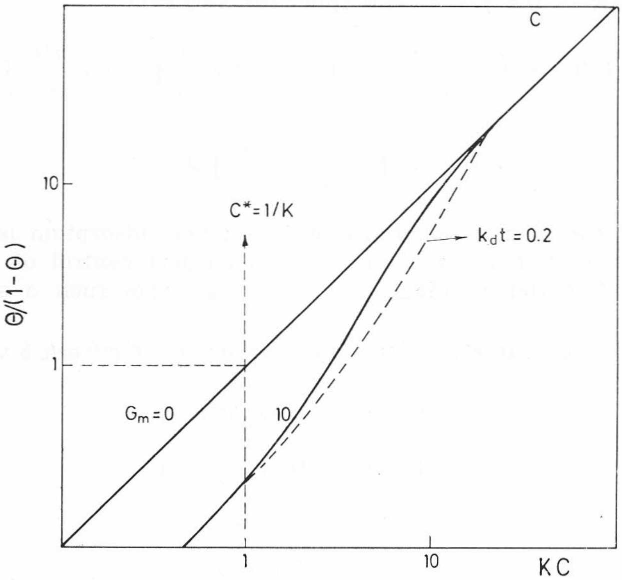

Figure 5. Plot of $\Theta/(1-\Theta)$ vs. C (KC for theoretical predictions) in a log-log diagram for the Langmuirian type of adsorption and two different values of $G_m = \Gamma_m K/\sqrt{Dt}$ (full lines $G_m = 0$ and 10) under equilibrium conditions as well as one plot for $k_d t = 0.2$ and $G_m = 0$ (dashed line). Obviously, the kinetic and diffusion controlled adsorption can be distinguished from the shape of these plots.

dependence of adsorption for some fatty acids at the mercury-sodium chloride interface suggested that adsorption of these substances proceeds in several steps including strong lateral interactions between the adsorbed molecules[51–53]. The extremely high FFG type of interaction coefficients suggests that there is a strong probability of new phase formation at higher times of adsorption. The final adsorption equilibrium in the case of valeric acid has not been attained up to three hours of adsorption[51–53]. Similar behaviour has been reported also for some polymeric adsorbates[13,82]. A theory of these processes has not yet been developed at a satisfactory level. A simple model of the first order secondary surface process has been developed recently[51]. Assuming the Langmuirian type of adsorption, such a model can be described by the following eqns:

$$KC_o = \Theta_1/(1-\Theta_1-\Theta_2) \quad \text{and} \quad d\Theta_2/dt = k_1\Theta_1 - k_2\Theta_2$$

where Θ_1 is the surface coverage for the first attachment of the adsorbate to the interface (very fast process), and Θ_2 the surface coverage for adsorbed molecules in the secondary transformed state (formed by a relatively slow process). The final adsorption equilibrium can then be described by the following relations:

$$\Theta_1 = k_1\Theta_1/k_2 \quad \text{and} \quad KC_o\,(1+k_1/k_2) = \Theta/(1-\Theta)$$

where $\Theta = \Theta_1 + \Theta_2$ and C_o is the volume concentration of adsorbate near the interface which can be obtained from the integral eqn. for mass transport[6]. In this way the total surface coverage can be obtained:

$$\Theta = \Theta_1^\infty + (1 - \Theta_1^\infty)\, k_1 \int \Theta_1\, e^{-\varepsilon(t-\tau)}\, d\tau$$

where

$$\Theta_1^\infty = KC_o/(1 + KC_o), \quad C_o = C^* (1 - I_o)$$

and

$$\varepsilon = k_1\Theta_1 + k_2, \quad I_o = (\Gamma_m K/C^* \sqrt{D}) \int \frac{d\,[C_o\,(1 - \Theta)]}{d\tau}\, \xi_o\,(1 - \tau)\, d\tau$$

In cases where $k_2 \gg k_1$, the final adsorption equilibrium involves only the secondary transition state of adsorbed molecules $\Theta \approx \Theta_2$ with the adsorption equilibrium constant Kk_1/k_2. Then measurable surface coverages are attained in conditions where $\Theta_1^\infty \approx KC_o$ and consequently:

$$\Theta \approx k_1 K \int C_o e^{-\varepsilon(t-\tau)}\, d\tau$$

and

$$\varepsilon \approx k_1 K C_o$$

The overall rate constant of adsorption is in this case equal to k_1K. The primary attachment to the interface represents an undetectable intermediate state of adsorption process and the overall process is equivalent to the case of single step adsorption kinetics. In the case of the FFG type of adsorption one can write the following eqns.[51]:

$$KC_o = \Theta_1 e^{b_{11}\Theta_1 + b_{12}\Theta_2}/(1 - \Theta_1 - \Theta_2)$$

and

$$d\Theta_2/dt = k_1\Theta_1 e^{-a_{11}\Theta_1 - a_{12}\Theta_2} - k_2\Theta_2\, e^{a_{21}\Theta_1 + a_{22}\Theta_2}$$

In cases where $k_2 \gg k_1$ and consequently $\Theta \approx \Theta_2$, these eqns. reduce to simpler forms:

$$KC_o \approx \Theta_1 e^{b_{12}\Theta}/(1 - \Theta)$$

and

$$d\Theta/dt \approx k_1 K C_o\,(1 - \Theta)\, e^{-(a_{12} + b_{12})\Theta} - k_a \Theta e^{a_{22}\Theta}$$

which is also equivalent to the case of a single step FFG type of adsorption kinetics. The mixed type of adsorption kinetics could be observed in this case only if the apparent strength of adsorption for the final state due to the intrinsic kinetics is comparable to the strength of the first attachment of the adsorbate to the interface because $\Theta_2 \approx \Theta$. The influence of mass transport on adsorption kinetics for these complex models can be obtained only by numerical methods.

CONCLUSIONS

The time dependence of adsorption can be controlled by intrinsic adsorption kinetics and mass-transport of the adsorbate from the bulk of homogeneous phase to the interface. Theoretical predictions suggest that the limit for the influence of mass transport by natural diffusion on the time dependence of adsorption can be expressed in the following way $G_m = \Gamma_m K/\sqrt{Dt} \approx \approx 0.1$. The strength of adsorption clearly has a profound influence on this limiting condition, because Γ_m and D do not vary significantly for different adsorbates. However, in the case of hydrodynamic contributions to the mass transport in the form of eddies of different time scales, diffusion coefficient D should be replaced by the so called dispersion coefficient which can be changed depending on the environment for many orders of magnitude. Therefore, the time dependence of adsorption in natural environment cannot be straightforwardly predicted from the results obtained in the laboratory. Although the rate of the first attachment of the adsorbate to the interface is assumed to be very high in many cases, the time dependence is observed also under the conditions when mass transport cannot control the adsorption process. For interpretation of the results obtained under such conditions a whole variety of rate laws have been developed corresponding to different types of adsorption equilibrium and surface equations of state. The rate constants obtained by fitting the experimental results with theoretical predictions obtained using a certain rate law are probably not intrinsic rate constants for the first attachment of the adsorbate from the homogeneous phase to the interface, but rather some overall parameters which are the results of a whole series of secondary surface processes. The model of adsorption which corresponds to the FFG type adsorption isotherm can be used for theoretical predictions for adsorption of most organic as well as some polymeric adsorbates at the solid-liquid interfaces. The same model could be used for the interpretation of metal ions at hydrous oxide surfaces. Several methods for the interpretation of experimental results using the FFG model of adsorption have been developed so far in literature. The type of adsorption isotherm can be selected very effectively on the basis of a plot of $\log(\Theta/C)$ vs. $\log(1-\Theta)$. Theoretical predictions are not very sensitive to the value of the kinetic coefficient λ, in the rate law corresponding to the FFG type of adsorption, which can therefore be set to the value of 0.5 without producing significant errors. Theoretical predictions about the limit of the influence of intrinsic adsorption kinetics on the time dependence of adsorption can be expressed as $k_d\,t = 10$ in the absence of mass transport on adsorption. This limit is shifted to higher $k_d\,t$ values if the mass transport plays a more significant role ($k_d\,t = 30$ for $G_m \approx 1$). Adsorption parameters can be determined from the comparison of theoretical predictions with experimental results in a plot of $\log \Theta e^{b^*\Theta}/(1-\Theta)$ vs. $\log C$ ($\log KC$ for theoretical predictions) where the b^* coefficient is selected arbitrarily in order to increase the accuracy of determination of a true FFG interaction coefficient »b«. The adsorption equilibrium constant K should be determined with great caution. The absence of the time dependence of adsorption should be supported by the shape of the adsorption isotherm in order to avoid possible errors which could appear in cases of a very slow establishment of the adsorption equilibrium. Any deviation of the shape of the adsorption isotherm from the one expected for the state of equilibrium indicates a need for additional experiments in a wider range of adsorption times. Sometimes, in a wide range of adsorption times different steps of the adsorption process can be observed which can complicate the interpretation of experimental results. Simple first order kinetic models of multistep adsorption have not been successful in predicting accurately enough this type of adsorption processes. Therefore, more complex models of surface processes should be developed in the future.

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SAŽETAK

Vremenska ovisnost adsorpcije na granici faza kruto-tekuće

I. Ružić

Raspravlja se o vremenskoj zavisnosti adsorpcije na granici faza čvrsto-tekuće za slučajeve kada je proces adsorpcije kontroliran transportom mase ili kinetikom adsorpcije. Pokazano je da vremenska ovisnost adsorpcije u slučaju adsorpcije kontrolirane transportom mase uglavnom ovisi o jakosti adsorpcije (prirodna difuzija), a ponekad i o koeficijentu transporta mase (koeficijentu disperzije za slučaj kada hidrodinamika kretanja medija dolazi do izražaja, kao što je to slučaj u prirodnom mediju). Za pravu kinetičku kontrolu procesa adsorpcije prikazan je čitav niz kinetičkih zakona. Prikazane su metode za interpretaciju eksperimentalnih rezultata. Spomenuta je također i mogućnost razlikovanja slučajeva kada je adsorpcija kontrolirana transportom mase ili kinetikom adsorpcije. Opisani su jednostavni modeli dvostepene adsorpcije gdje je prvi stupanj prethodno vrlo brzo prianjanje adsorbiranih molekula uz granicu faza. Zaključeno je da za ispravnu interpretaciju eksperimentalnih rezultata utisak da je adsorpcija u uvjetima ravnoteže treba obvezno potvrditi detaljnim proučavanjem oblika adsorpcijske izoterme. U neravnotežnom slučaju potrebno je proširiti mjerenja adsorpcije na širu vremensku skalu.