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Theoretical description of the kinetics of solute adsorption at heterogeneous solid/solution interfaces

On the possibility of distinguishing between the diffusional and the surface reaction kinetics models

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Abstract

The kinetics of adsorption at solid/liquid interfaces is of crucial importance for life on our planet and a variety of technological processes. Let us remark, for instance, that the oxide/electrolyte interface is the largest natural interface existing on the earth. It is very impressive to observe the growing number of the papers reporting on application of adsorption processes in the technologies of environmental protection. The purification of wastewaters, for instance, has become one of the largest industries now. To optimize the cost and performance of the adsorption technology, one has to consider both the costs of sorbents, and the efficiency of the adsorption process. That efficiency is related not only to the equilibrium features of an adsorption system but also to the kinetics of the adsorption process. In technological processes a sorbent and a solution are brought into contact for a limited period of time, so, the rate of the transport of solute molecules from the bulk to the adsorbed phase is here of a primary importance. According to some generally expressed views a sorption process can be described by four consecutive kinetic steps:

1. transport in the bulk solution;
2. diffusion across the film surrounding the sorbent particles;
3. diffusion in the pores of the sorbent;
4. sorption and desorption on the solid surface viewed as a kind of chemical reaction.

One of these steps is the slowest and controls the rate of sorption. Depending on the assumption which of these steps is the rate-controlling one, a variety of equations have been proposed in literature to describe that kinetic step. The knowledge of the nature of that kinetic and its theoretical description are very crucial for practical applications, as a key to design the adsorption equipment and conditions for an optimum efficiency to be achieved.

So, first some laboratory experimental tests and next their subsequent theoretical analyses are carried out to elucidate the nature of the rate-controlling kinetic process. Such studies may involve a variety of experiments whose time dependence of adsorption is the most fundamental information. Sometimes accompanying studies of the corresponding adsorption equilibria are also carried out, but it seems that the importance of these studies has not been sufficiently recognized.

Only such combined study creates a chance to distinguish correctly between one and another kinetic model to be assumed. However, the most essential condition is using proper theoretical expressions to represent the features of some kind of kinetics. Here we will show how the above-mentioned conditions may affect distinguishing between the kinetics which is governed by the intraparticle diffusion, and that in which surface reactions control the rate of sorption in an adsorption system. This is because these two kinetic models are most frequently assumed in the theoretical interpretation of experimental kinetic data.

Keywords: Adsorption; Kinetics; Intraparticle diffusion; Surface reaction

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1. Introduction

As we mentioned in the previous section, the majority of the recently published papers report on the kinetics of sorption of various solutes which are contaminants of wastewaters. The large industrial scale of water purification involves the necessity of using sorbents which are cheap and widely available materials, to reduce costs of these large-scale industrial processes. It appears then that such typical cheap, widely available materials are sorbents with highly irregular surfaces. These are usually porous surfaces, characterized by strong geometric, chemical and energetic surface heterogeneity, which makes the theoretical description of adsorption on these surfaces a very difficult task. Nevertheless, the technological importance of these materials creates a necessity of finding theoretical description of kinetics of sorption by such sorbents.

Impressive progress has been made during the last few decades in the theoretical description of adsorption equilibria in such systems. Here a variety of adsorption isotherm equations have been proposed, and some of them have become very popular. Most of them were proposed as modification of the classical Langmuir equation, which is known to describe one-site-occupancy adsorption on an energetically homogeneous lattice of adsorption sites. Therefore, for our further consideration it is worth mentioning the theoretical principles of the Langmuir model of adsorption. The chemical potential of the adsorbed (solute) molecules is then given by the expression:

$$\mu_{\mathrm{s}} = kT \ln \frac{\theta}{1-\theta} - kT \ln q_{\mathrm{s}}, \tag{1}$$

where $\theta = N_{\mathrm{t}}/N_{\mathrm{m}}$ is the fractional coverage of adsorption sites by N_{t} adsorbed molecules; N_{m} the total number of adsorption sites on the solid surface; q_{s} the molecular partition function of the adsorbed molecules; k and T are the Boltzmann constant and temperature, respectively. When the chemical potential of the solute molecules in the bulk solution is assumed to have the following form:

$$\mu_{\mathrm{b}} = \mu_{\mathrm{b}}^{\circ} + kT \ln c, \tag{2}$$

one arrives at the Langmuir isotherm at equilibrium:

$$\theta^{(\mathrm{e})} = \frac{K_{\mathrm{L}} c^{(\mathrm{e})}}{1 + K_{\mathrm{L}} c^{(\mathrm{e})}}, \tag{3}$$

in which

$$K_{\mathrm{L}} = q_{\mathrm{s}} \exp\left(\frac{\mu_{\mathrm{b}}^{\circ}}{kT}\right), \tag{4}$$

and the superscript (e) refers to equilibrium. In the case of real energetically heterogeneous solid surfaces, q_{s} varies from one to another site characterized by an adsorption energy ε,

$$q_{\mathrm{s}} = q_{\mathrm{s}}^{\circ} \exp\left(\frac{\varepsilon}{kT}\right), \tag{5}$$

and the experimentally monitored total surface coverage $\theta_{\mathrm{t}}^{(\mathrm{e})}$ is then given by the following average [1,2]:

$$\theta_{\mathrm{t}}^{(\mathrm{e})} = \int_{\varepsilon_{\mathrm{l}}}^{\varepsilon_{\mathrm{m}}} \frac{Kc^{(\mathrm{e})} \exp(\varepsilon/kT)}{1 + Kc^{(\mathrm{e})} \exp(\varepsilon/kT)} \chi(\varepsilon)\, \mathrm{d}\varepsilon, \tag{6}$$

In Eq. (6), $K_{\mathrm{L}} = K \exp(\varepsilon/kT)$ and $\chi(\varepsilon)$ is the distribution of adsorption sites among adsorption energy values ε, normalized to unity. Further, ε_{l} and ε_{m} are the lowest (l) and the maximum (m) values of the adsorption energy ε on the lattice of adsorption sites (local minima in the potential of solute–surface interactions).

By considering the surface heterogeneity one might expect a large variety of adsorption behaviour to be observed. Surprisingly, it appears that, to the first approximation, the majority of all the reported experimental adsorption isotherms can be correlated fairly well using a number of simple empirical isotherms [2,3]. These have been, for instance, the Freundlich isotherm, applicable at low surface coverages, next its generalized form – the Langmuir–Freundlich isotherm, applicable also at higher surface coverages, and the Dubinin–Radushkevich isotherm used to describe adsorption on microporous surfaces. The above three empirical isotherms seemed to describe well enough general features of the majority of adsorption systems in the region of submonolayer coverage. This observation led Cerofolini, Rudzinski and Everett to postulate existence of a certain universal function $\chi(\varepsilon)$ that would describe some general features of the adsorption energy distribution of real solid surfaces. Individual features of an adsorption system should be reflected in the values of parameters appearing in that universal function. However, the analytical form of that adsorption energy distribution should be the same for all the really existing surfaces. This theoretical development of that generalized adsorption energy distribution was based on assuming a model of a geometrically distorted solid surface and on using simple thermodynamic arguments. Assuming that this generalized function represents $\chi(\varepsilon)$ in the integral equation (6) led Rudzinski et al. to a generalized adsorption isotherm equation, which should describe adsorption on all the real, energetically heterogeneous surfaces. Depending on the values of parameters and the assumed adsorption regime (pressure, coverage), that generalized adsorption isotherm reduced practically to the Langmuir–Freundlich isotherm, the Freundlich isotherm or to the Dubinin–Radushkevich isotherm. That general isotherm suggested also possibility of observing behaviours which might be described by other simple isotherm expressions, like the Toth empirical isotherm, for instance.

However, no general relationships have been known yet, which would create links between general features of the adsorption energy distribution of the real solid surfaces and general features of their surface geometric heterogeneity, described by the pore size distribution. Meanwhile, the existence of such a general function describing the character of pore size distribution of all the real porous solid surfaces has already been postulated in literature by the assumption of a fractal nature of real solid surfaces. Then Rudzinski et al.