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On the applicability of the pseudo-second order equation to represent the kinetics of adsorption at solid/solution interfaces: a theoretical analysis based on the statistical rate theory

Władysław Rudzinski · Wojciech Plazinski

Abstract It is shown that the empirical pseudo-second order kinetic equation is a very efficient formula to correlate the kinetic data generated by applying theoretical expressions developed from the fundamental SRT (Statistical Rate Theory) approach to the interfacial transport. This is especially true when the most popular linear representation is used in which time/adsorbed amount is plotted vs. time. However, the commonly observed goodness of such linear plots does not necessarily speak for the applicability of the pseudo-second order kinetic equation. A reliable estimation, for instance, of the equilibrium adsorbed amount is possible only when a substantial part of a kinetic isotherms corresponds to the conditions close to equilibrium. Energetic surface heterogeneity increases the goodness of these linear regressions. Then, experimental errors have only little effect on the pseudo-second linear plots.

Keywords Statistical rate theory · Adsorption · Kinetics · Pseudo-second order equation · Estimating the equilibrium adsorbed amount

Nomenclature

c	Actual (time-dependent) sorbate concentration in the bulk phase
c_{in}	Initial sorbate concentration in the bulk phase
c_e	Equilibrium sorbate concentration in the bulk phase
f, $f_{\min}$	Coefficients defined in (16) and (21), respectively
k_2	Pseudo-second order constant
K_L	The Langmuir constant
K'_{ls}	Rate of exchange at equilibrium in the SRT equation
N_m	Monolayer capacity
t	Time
V	Volume of the bulk solution
α, γ	Heterogeneity parameters
ε	Energy of adsorption
$\varepsilon_m, \varepsilon_l$	The lowest (l) and the maximum (m) values of the adsorption energy
λ	Coefficient defined in (7)
μ_b, μ_s	Chemical potentials of the sorbate in the bulk (b) and the adsorbed (s) phases
$\theta, \theta(t), \theta(\tau)$	Time-dependent surface coverage
θ_e	Surface coverage at equilibrium
τ	Dimensionless time defined in (7)
$\tau_f, \tau_{f_{\min}}$	Characteristic values of dimensionless time defined in (16) and (21)

1 Introduction

The pseudo-second order kinetic equation (Blanchard et al. 1984; Ho and McKay 1999, 2000) is probably now the most frequently used expression to correlate experimental data for kinetics of adsorption at the solid/solution interfaces. Most commonly its integral form is applied, which predicts that the ratio of the time/adsorbed amount should be a linear function of time. Indeed, such highly linear

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This article is dedicated to Professor Mietek Jaroniec on the occasion of his 60th birthday.

W. Rudzinski
Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Cracow, Poland

W. Rudzinski (✉) · W. Plazinski
Department of Theoretical Chemistry, Faculty of Chemistry, UMCS, pl. M. Curie-Sklodowskiej 3, 20-031 Lublin, Poland
e-mail: rudzinsk@hermes.umcs.lublin.pl

plots have been reported for a large variety of adsorption systems and conditions applied in a kinetic experiment (Ho and McKay 1999; Wan Ngah and Hanafiah 2008; Grimm et al. 2008; Ho 2006a; Hameed and Hakimi 2008; Aydın et al. 2008). In view of the success of that empirical kinetic equation, it may surprise one that so little has been done so far to study the theoretical background of the pseudo-second order kinetic equation (Azizian 2004, 2006; Rudzinski and Plazinski 2006; Liu 2008).

It has been only very recently when such efforts were attempted by Azizian (2004) applying for that purpose the classical Theory of Activated Adsorption/Desorption. Next, Rudzinski and Plazinski (2006) started such fundamental research based on the new approach to interfacial kinetics called the Statistical Rate Theory. We have focused our attention on solid/solution systems with strongly heterogeneous solid surfaces. Our theoretical studies seemed to suggest that the pseudo-second order kinetic equation is a formula that simulates well the behaviour predicted theoretically for such systems:

$$\frac{d\theta(t)}{dt} = 2\sigma(\theta_e - \theta(t)) + \frac{1}{3}\sigma^3(\theta_e - \theta(t))^3 + \frac{1}{60}\sigma^5(\theta_e - \theta(t))^5 + \cdots. \tag{1}$$

In the above equation $\theta(t)$ is the surface coverage at a certain time t, θ_e is the amount adsorbed at equilibrium and σ is a coefficient having a clear physical interpretation on the ground of the SRT.

When the terms $(\theta_e - \theta)$ of the order higher than three can be neglected, the pseudo-second order equation may be considered as a hybrid between the first and the third terms whose hybrid might simulate well the behaviour predicted by this theoretical expression. Moreover, it can be shown in a rigorous way that for the full form of expression one has: $\lim_{t\to\infty}(t/\theta(t))/t = 1/\theta_e$. It means that when the linear regression time/adsorbed amount vs. time is made for the kinetic data points measured close to the equilibrium, one should correctly determine the amount adsorbed at equilibrium. This problem will be subjected here to our more profound analysis in which also homogeneous and moderately heterogeneous surfaces will be taken into consideration.

2 Theory

2.1 The principles of the statistical rate theory for the kinetics of adsorption on homogeneous solid surfaces

Statistical Rate Theory (SRT) belongs to the family of approaches which relate the rate of adsorption/desorption to the chemical potentials of the sorbate molecules in the bulk (μ_b) and the adsorbed (μ_a) phase. This approach was first proposed in literature by Ward et al. (1982). It was successfully applied to describe the rates of interfacial transports of various kinds. Very recently the SRT has been also used to describe the kinetics of solute adsorption at the solid/solution interfaces (Rudzinski and Plazinski 2006, 2007a, 2007b, 2008a, 2008b, 2008c; Azizian et al. 2008). Following SRT:

$$\frac{d\theta}{dt} = K'_{ls}\left[\exp\left(\frac{\mu_b - \mu_a}{kT}\right) - \exp\left(\frac{\mu_a - \mu_b}{kT}\right)\right], \tag{2}$$

K'_{ls} is the rate of adsorption/desorption at equilibrium, whereas k and T denote the Boltzmann constant and absolute temperature, respectively. Recently we have shown that when the Langmuir model of adsorption onto a homogeneous surface is accepted, expression (2) takes the following form (Rudzinski and Plazinski 2007a):

$$\frac{d\theta}{dt} = K'_{ls}\left[K_L c\frac{1-\theta}{\theta} - \frac{1}{K_L c}\frac{\theta}{1-\theta}\right] \tag{3}$$

in which c is the time-dependent sorbate concentration in the bulk phase and K_L is the Langmuir constant. When the equilibrium is assumed to be reached, i.e. $d\theta/dt = 0$, then, (3) leads to the Langmuir isotherm equation:

$$\theta_e = \frac{K_L c_e}{1 + K_L c_e}. \tag{4}$$

The subscript e will always denote equilibrium conditions here.

The relation $K'_{ls} = K_{ls}c_e(1-\theta_e)$ is usually accepted due to the proportionality of the bulk/surface frequency of collisions of the solute molecules with the free available surface sites.

The K_L constant can be expressed through the value of the equilibrium surface coverage θ_e. Then, expression (3) can be rewritten to:

$$\frac{d\theta}{dt} = K_{ls}c_e(1-\theta_e)\left[\frac{c(1-\theta)\theta_e}{c_e(1-\theta_e)\theta} - \frac{c_e(1-\theta_e)\theta}{c(1-\theta)\theta_e}\right]. \tag{5}$$

This simple procedure of expressing some constants appearing in the SRT kinetic equation through the equilibrium surface coverage can also be applied in the case of other models of adsorption, taking into account surface heterogeneity, for instance. The advantages of applying such a procedure are following:

- reducing the number of the parameters which have to be estimated from the experimental equilibrium isotherm; this is especially important when (i) the kinetic experiment is not accompanied by the equilibrium one or (ii) when the experimental error is supposed to be significant in the case of equilibrium isotherm.

- the possibility of estimating the actual values of the equilibrium surface coverage when the experimental kinetic isotherms are at disposal.

The changes of the sorbate concentration with time can be expressed by the simple mass-balance equation:

$$c = c_{in} - N_m\theta/V \tag{6}$$

in which c_{in} is the initial sorbate concentration in the bulk phase, V is the volume of the solution and N_m is the monolayer capacity, i.e. the number of binding surface sites expressed as the maximum amount that can be adsorbed. For the purpose of our further considerations we introduce the following dimensionless parameters:

$$\begin{cases} \lambda = c_{in}V/N_m, \\ \tau = K'_{ls}t = K_{ls}c_e(1-\theta_e)t. \end{cases} \tag{7}$$

The value of λ parameter can vary from θ_e to infinity. When $\lambda \to \infty$, it means that the sorbate concentration in the bulk phase is practically constant during the kinetic experiment (adsorption system in which such a situation takes place was called by us the "volume dominated" system). The case when almost all the sorbate is removed from the solution during an experiment is illustrated by the relation $\lambda \to \theta_e$. Then, SRT equation (5) can be rewritten to the following form:

$$\frac{d\theta}{d\tau} = \frac{\theta_e(\lambda-\theta)(1-\theta)}{\theta(\lambda-\theta_e)(1-\theta_e)} - \frac{\theta(\lambda-\theta_e)(1-\theta_e)}{\theta_e(\lambda-\theta)(1-\theta)}. \tag{8}$$

2.2 The rate of adsorption on strongly energetically heterogeneous surfaces

In the case of strongly energetically heterogeneous surface there is often assumed a broad dispersion of adsorption energies, described by the following rectangular function:

$$\chi(\varepsilon) = \begin{cases} \frac{1}{\varepsilon_m-\varepsilon_l}, & \text{for } \varepsilon_l \le \varepsilon \le \varepsilon_m, \\ 0, & \text{elsewhere}. \end{cases} \tag{9}$$

The ε_l and ε_m parameters are the lowest (l) and the maximum (m) values of the adsorption energy ε on a heterogeneous lattice of adsorption sites. This simple rectangular function, combined with the Condensation Approximation method can be applied to arrive at the Temkin equilibrium adsorption isotherm (Rudzinski and Everett 1992; Rudzinski and Plazinski 2006).

The general rate equation corresponding to the function (9), developed by using the SRT approach, is the Elovich-like, kinetic expression (Rudzinski and Plazinski 2006, 2007a):

$$\frac{d\theta}{d\tau} = \frac{\lambda-\theta}{\lambda-\theta_e}\exp\left[\gamma(\theta_e-\theta)\right] - \frac{\lambda-\theta_e}{\lambda-\theta}\exp\left[-\gamma(\theta_e-\theta)\right], \tag{10}$$

where γ is the heterogeneity parameter, defined as: $\gamma = (\varepsilon_m - \varepsilon_l)/kT$. The principles of arriving at (10) were described in our previous paper (Rudzinski and Plazinski 2006). In that paper we also launched an idea that the Taylor expansion (1) of the r.h.s. of (10) around $\theta = \theta_e$, cut after the third order term, might simulate well the behaviour characteristic of the pseudo-second order kinetic equation. As noticed by Liu and Shen (2008) and Liu (2008), "the pseudo second-order kinetic equation cannot be naturally obtained" from (1) and (10). It is basically true if considering the direct, mathematical derivation and the concept of sorption reaction order. However, our idea was to launch an opinion that expression (10) simulates well the "pseudo-second order behaviour". Here, we are going to study some features of the SRT expressions (8) and (10) related to that problem. First, the case of a constant sorbate concentration will be considered, i.e. $c = c_{in} = c_e$.

While neglecting the second term on the right-hand-side of (10), responsible for the rate of desorption, one can arrive at the differential form of the popular Elovich equation:

$$\frac{d\theta}{d\tau} = \exp\left[\gamma(\theta_e-\theta)\right]. \tag{11}$$

The integral form of the Elovich equation is obtained after solving (11) with the boundary condition $\theta(\tau=0)=0$:

$$\theta(\tau) = \theta_e + \frac{1}{\gamma}\ln(e^{-\gamma\theta_e} + \gamma\tau). \tag{12}$$

When the kinetics is described by (12), one can easily observe the non-physical behaviour of this formula, i.e. for longer adsorption times we have: $\lim_{\tau\to\infty}\theta(\tau) = \infty$. This is due to neglecting the second term in (10) which accounts for the rate of simultaneously occurring desorption. Thus, (10) can be treated as a more general form of the Elovich equation, which can also be applied at longer adsorption times.

When the boundary condition $\theta(\tau=0)=0$ is accepted, the integral form of the general equation (10), obtained for the case of a constant sorbate concentration in the bulk phase, i.e. when $\lambda \to \infty$, can be written in the following form (Rudzinski and Plazinski 2006):

$$\theta(\tau) = \theta_e - \frac{1}{\gamma}\ln\left[\coth(\operatorname{arc\,coth} e^{\gamma\theta_e} + \gamma\tau)\right]. \tag{13}$$

In contrast to the Elovich equation, expression (13) takes a finite value in the limit $\tau \to \infty$, equal to the equilibrium surface coverage: $\lim_{\tau\to\infty}\theta(\tau) = \theta_e$.

2.3 The pseudo-second order rate equation

The pseudo-second order equation assumes that the rate of adsorption can be represented by the following expression (Ho and McKay 2000):

$$\frac{d\theta(t)}{dt} = k_2(\theta_e - \theta(t))^2, \tag{14}$$

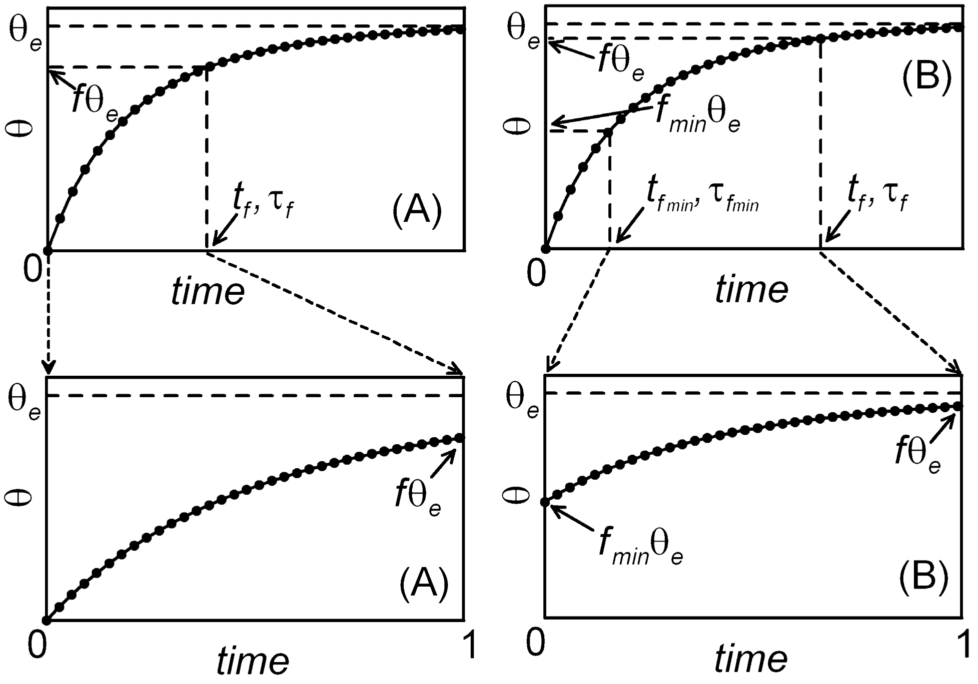

Fig. 1 A symbolic illustration of the meaning of the f and $f_{\min}$ coefficients. Other details can be found in the text

in which k_2 is a constant, which can be determined from the following linear correlation of experimental data:

$$\frac{t}{\theta(t)} = \frac{1}{\theta_e} t + \frac{1}{k_2 \theta_e^2}. \tag{15}$$

Equation (15) is the integral form of (14), obtained by assuming the boundary condition $\theta(t = 0) = 0$. It should be emphasized that relation (15) is not the only possible form of linear representation that can be obtained for the pseudo-second-order equation (Ho 2006b). However, it is the most popular one, thus, it will be applied in our further studies. Both theoretical investigations (Azizian 2004; Rudzinski and Plazinski 2006) and the experimental studies (Ho and McKay 1998a, 2000) indicate that the value of k_2 constant usually depends on the initial sorbate concentration in the bulk phase. As it has been recently proved (Azizian 2004), the pseudo-second order equation can be derived by assuming significant changes in the bulk solute concentration and applying the classical Theory of Activated Adsorption/Desorption approach (Langmuirian kinetics (Langmuir 1918)). In 2006 Rudzinski and Plazinski proposed their first interpretation of (14) based on the SRT approach to adsorption/desorption kinetics.

For the purpose of our further investigations, we introduce the additional parameter f, defined as:

$$f = \frac{\theta(t = t_f)}{\theta_e} \quad \text{or} \quad f = \frac{\theta(\tau = \tau_f)}{\theta_e}, \tag{16}$$

where t_f and τ_f are the times at which the ratio $\theta/\theta_e = f$. The kinetic isotherms of adsorption can be treated as monotonic functions, so, the value of f defines t_f or τ_f. The f parameter can be also described as a degree of reaching the equilibrium state by an adsorption system after elapsing of a certain period of time. Of course, the value of this parameter can vary within the range (0; 1), depending on how close to equilibrium the adsorption system is. The adsorption times monitored in different experiments may differ by several orders of magnitude, depending on the physical nature of an adsorption system. In order to avoid this complication we made the two following assignments: $t_f = 1$ and $\tau_f = 1$. The idea of using f coefficients is illustrated symbolically in part (A) of Fig. 1.

Thus, it can be easily proved that the k_2 constant (playing a role of time-scaling factor) might be unequivocally defined by the f parameter in the following way:

$$k_2 = \frac{f}{(1 - f)\theta_e}. \tag{17}$$

Then, the integral form of the pseudo-second order equation (15) can be rewritten to:

$$\theta(t) = \frac{\theta_e f t}{1 - f + f t}. \tag{18}$$

The idea that the pseudo-second order equation is a simplified form of the SRT expression (13) can be quantitatively proved by comparing the basic features of these two equations. In our previous papers we have shown that the plots of both SRT equations (8) and (10) presented in the form suggested by (15), i.e. as τ/θ vs. τ, exhibit a highly linear behaviour. This observation has been confirmed for a wide range of λ and γ parameter values. The details can be found in the papers by Rudzinski and Plazinski (2006, 2007b).

3 Calculations

3.1 The comparison of the pseudo-second order equation and the SRT expressions

In the first step, we are going to compare the behaviour of the pseudo-second order rate equation with that of the Elovich equation.

In order to compare the behaviour of the kinetic isotherms, we simply generated numerically the points $(t;\theta)$ by using the pseudo-second equation (18) and accepting certain values of f and θ_e parameters. Next, we fitted these generated plots by the Elovich equation (12), and by treating γ and $K'_{ls}e^{\gamma\theta_e}$ as the best-fit parameters (these parameters have been chosen to minimize the number of best-fit parameters). The number of generated $(t;\theta)$ points was, in all the cases presented here, equal to 1000. The results of our calculations are presented in Figs. 2 and 3.

Our model investigation shows that the behaviour of an adsorption system predicted by both equations (12) (Elovich) and (18) (pseudo-second order) may be very similar when certain conditions are fulfilled. Namely, the differences between the Elovich equation and the pseudo-second order equation are practically negligible when the value of f parameter is not higher than about 0.6. This can be seen in Fig. 2. The deviations become more and more significant when taking into account surface coverages close to their equilibrium values (i.e. when the value of f parameter is close to 1). Figure 2 shows that such situation occurs when $f > 0.7$. The assumed value of the equilibrium surface coverage was $\theta_e = 0.5$. However, Fig. 3 shows that the quality of the fits presented there is not sensitive to the accepted value of θ_e.

As the Elovich and the pseudo-second order equations belong to the most popular and the most commonly-applied formulas, we decided to perform a more detailed analysis concerning the physical interpretation and the correlations between the parameters appearing in these equations. This is described in Appendix A.

In order to find out whether the unphysical behaviour of the expression (12) (when $t \to \infty$) might not be responsible for the deviations between the Elovich and the pseudo-second order equations, when the value of f is large, we repeated the procedure of generating pseudo-experimental data, using the pseudo-second order equation (18). Then, we fitted the numerically generated points $(t;\theta)$ by using the SRT equation (13). In each case γ, $K'_{ls}e^{\gamma\theta_e}$ and $K'_{ls}e^{-\gamma\theta_e}$ were treated as the best-fit parameters. The results of these model calculations are presented in Figs. 4 and 5.

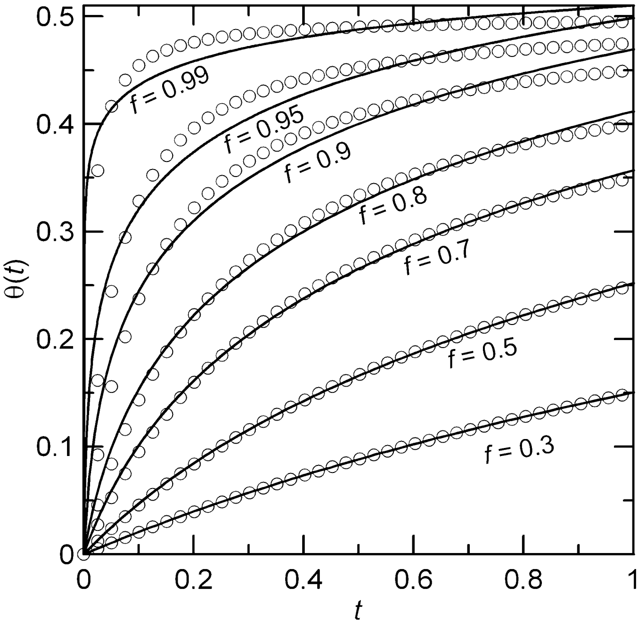

Fig. 2 Pseudo-second order kinetic isotherms (○) calculated from (18) and fitted (——) by the Elovich equation (12). The calculations were performed for the equilibrium surface coverage $\theta_e = 0.5$ and for seven different values of f parameter

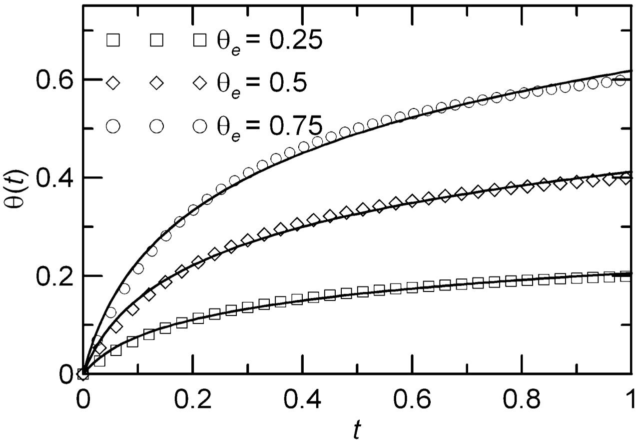

Fig. 3 Pseudo-second order kinetic isotherms (○, □, ◇) calculated from (18) and fitted (——) by the Elovich equation (12). The calculations were performed for the value of f parameter at which the differences between the Elovich equation and the pseudo-second-order equation become significant, i.e. for $f = 0.8$

Figure 4 shows that the SRT equation (13) can simulate very well the behaviour predicted by the pseudo-second order equation for a wide range of f parameter values. The significant differences between these two equations appear only when $f > 0.9$, i.e. when kinetic isotherms are monitored at extremely long times. Moreover, as in the case of the Elovich equation, the agreement between (13) and (18) seems to be independent of the value of the equilibrium surface coverage. This is presented in Fig. 5. However,

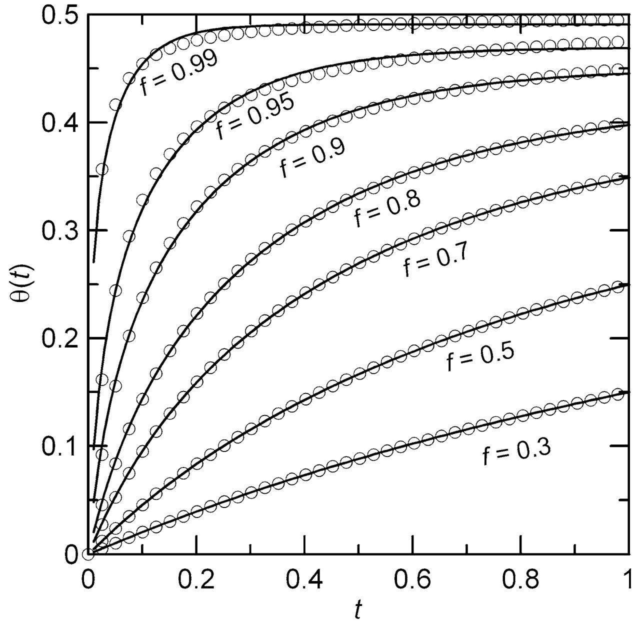

Fig. 4 The pseudo-second order kinetic isotherms (∘) calculated from (18) and fitted (——) by the SRT equation (13) (——). The calculations were performed for the equilibrium surface coverage $\theta_e = 0.5$ and for seven different values of parameter f

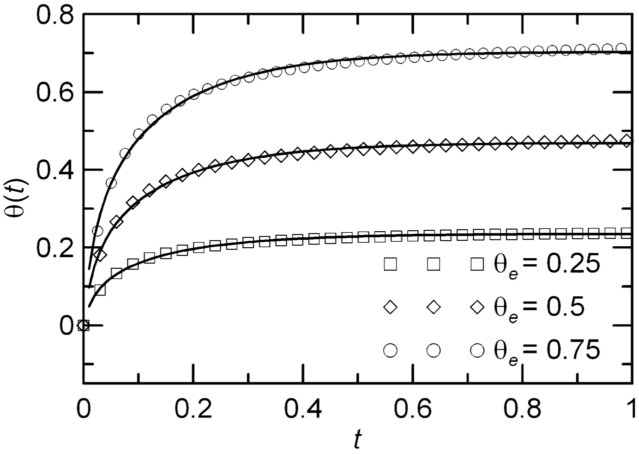

Fig. 5 The pseudo-second order kinetic isotherms (◇, □, ∘) fitted (——) by the SRT equation (13). The calculations were performed for the value of f parameter for which the significant differences between (13) and the pseudo-second-order equation (18) can be observed, i.e. for $f = 0.95$

we would like to note that the most popular method of applying (14) is the so-called pseudo-second order plot, represented by (15). The theoretical interpretation of the tangent of such liner plots is: $1/\theta_e$. The meaning of the tangent of the pseudo-second-order linear plots on the ground of our kinetic equation (13) is very similar. While studying the asymptotical behaviour of this expression one can show that (Rudzinski and Plazinski 2006):

$$\lim_{\tau\to\infty}\frac{\tau/\theta(\tau)}{\tau} = \lim_{\tau\to\infty}\frac{1}{\theta(\tau)} = 1/\theta_e. \tag{19}$$

It can be deduced that the interpretation of the tangent of the linear plot (15) which comes from every kinetic isotherm equation having the physical limit $\lim_{t\to\infty}\theta(t) = \theta_e$ is the same as that presented in (19). This fact can play an important role in the analysis of the experimental kinetic data. Namely, it means that the value of the equilibrium surface coverage can be determined from the pseudo-second order plot independently of the kinetic mechanism which governs the adsorption process. The only essential condition which has to be fulfilled is that a significant part of kinetic data must be monitored at the times when the adsorption system is close to equilibrium. This issue will be discussed in detail in the next subsection.

The above discussed simple method of determining θ_e value was successfully applied by us in our previous papers (Rudzinski and Plazinski 2007a).

3.2 The applicability of the pseudo-second order plots to determine the equilibrium surface coverage values

The pseudo-second order equation has been extensively used to correlate the experimentally monitored kinetic isotherms (Ho 2004). However, the compatibility of the θ_e values obtained by using relation (15) with the actual, measured, equilibrium surface coverages was investigated only for the case of a few selected adsorption systems (Ho and McKay 1998b, 1998c). The general, asymptotical behavior (19) suggests performing similar studies based on some fundamental theories of adsorption kinetics. Here, the statistical rate theory is applied.

The rate equation (8) is assumed to describe the adsorption kinetics onto a homogeneous solid surface. When surface heterogeneity is to be taken into account, the rate of adsorption may well be represented by the following expression, which was originally derived by Rudzinski and Plazinski (2007b):

$$\frac{d\theta}{d\tau} = \frac{(\lambda-\theta)(1-\theta)^{1/\alpha}\theta_e^{1/\alpha}}{(\lambda-\theta_e)(1-\theta_e)^{1/\alpha}\theta^{1/\alpha}} - \frac{(\lambda-\theta_e)(1-\theta_e)^{1/\alpha}\theta^{1/\alpha}}{(\lambda-\theta)(1-\theta)^{1/\alpha}\theta_e^{1/\alpha}}. \tag{20}$$

This is because (10) was derived by assuming the adsorption energy distribution (9) which contains two discontinuity points at ε_l and ε_m. This fact may lead to some inaccuracies in the obtained kinetic isotherms. Equation (20) can be derived by using the Gaussian-like adsorption energy distribution function which represents the surface heterogeneity in the case of the popular Langmuir-Freundlich equilibrium isotherm equation. Let us also note that, for physical reasons, the values of the heterogeneity parameter α can vary from 0 to 1 (i.e. the degree of heterogeneity increases when the value of α decreases) (Rudzinski and Everett 1992).

The main goal of our investigations is to study the applicability of the pseudo-second order plots to determine the equilibrium surface coverage. The values of θ_e obtained from the linear relation τ/θ vs. τ (see (15)), i.e. "θ_e calculated" are compared with those appearing in (8) and (20) i.e. with the "real" θ_e values. It is worth mentioning that when some "real" θ_e value is accepted, one can represent the technical conditions of the experimental system (solid/solution ratio) through changing the value of λ parameter and the degree of heterogeneity (in the case of (20)) by changing the α value. The coefficient of determination r^2 was always used to characterize the quality of all linear fits. Two competitive approaches have been applied here by us.

3.2.1 *Approach A*

In this approach the first step of the applied procedure is similar to that described in Sect. 2.1. Thus, we generated numerically the points $(\tau;\theta)$ using the SRT equations (8) or (20) and accepting certain values of f and θ_e parameters. The "degree of reaching the equilibrium", f, is again defined by (16). The assignment: $\tau_f = 1$ was kept, thus, the values of the dimensionless time τ can vary from 0 to 1. Next, the pseudo-second order plots were generated using transformation $(\tau,\theta) \to (\tau,\tau/\theta)$ and a simple linear regression was performed for each plot. The results of such regression were (i) the reciprocal of tangent, i.e. "θ_e calculated" (see (19)) and (ii) coefficient of determination, r^2.

All the calculations were performed for three values of the "actual" equilibrium surface coverage, three values of λ parameter and three values of α parameter (situation when $\alpha = 1$ corresponds to a homogeneous solid surface). The number of generated $(\tau;\theta)$ points was always equal to 1000. The results of our calculations performed for both homogeneous and heterogeneous surfaces are presented in Figs. 6–8.

This approach is essentially identical with the commonly applied procedures for analyzing the experimental kinetic data by using the pseudo-second order plots. It means that linear representation is used for all measured $(t;\theta)$ experimental points and the reciprocal of the tangent obtained in this way is often treated as the "real" equilibrium surface coverage.

The results presented in Figs. 6–8 can be summarized as follows:

- The application of Approach A leads to correct values of θ_e only for high values of f parameter; this means that, to obtain the results close to the correct ones, one must have at disposal experimental points measured at least at $\theta = 0.75\theta_e$.
- It appears that the obtained values of θ_e can either be lower or higher than the actual ones; it depends on the value of f parameter. Generally, it can be said, that at low values of f one arrives at θ_e values substantially lower than the actual ones.
- The above mentioned observations are valid for every solid/solution ratio (i.e. for any value of λ parameter) and/or degree of surface heterogeneity.
- The quality of the obtained linear fits always increases with the increasing value of θ_e.

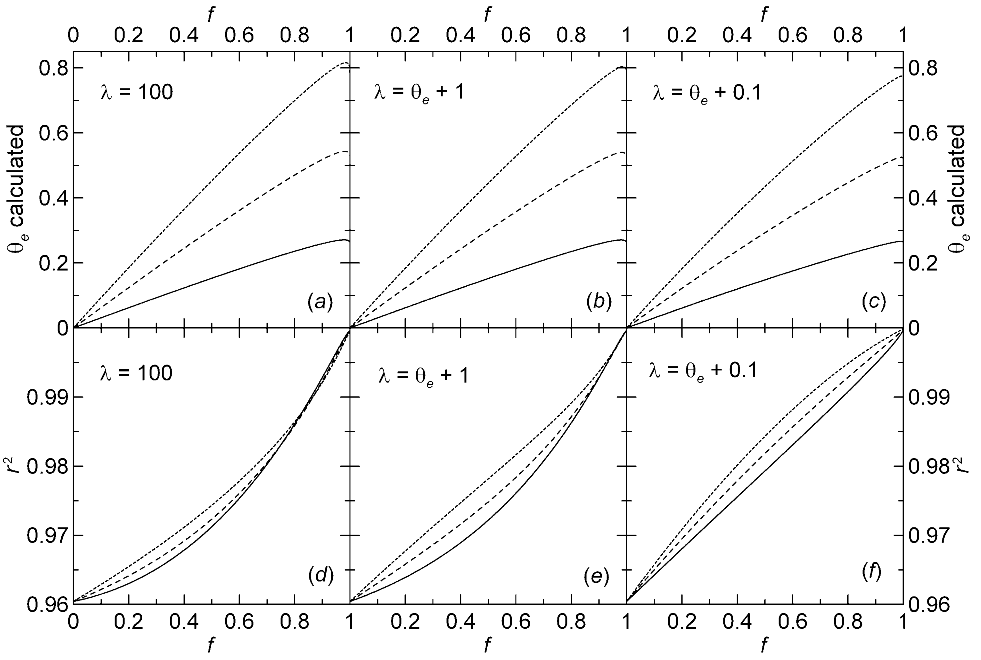

Fig. 6 Approach A. The results of the linear fitting of the pseudo-second order plots generated by using the SRT equation (8) representing the rate of adsorption onto a homogeneous surface. The calculations were performed for three different values of λ parameter and three values of equilibrium surface coverages: $\theta_e = 0.25$ (——), $\theta_e = 0.5$ (– – –) and $\theta_e = 0.75$ (- - - - -). The changes of calculated θ_e values (i.e. reciprocal of the tangent determined from linear regression) are presented in panels (**a**), (**b**) and (**c**) while the corresponding r^2 values are shown in panels (**d**), (**e**) and (**f**)

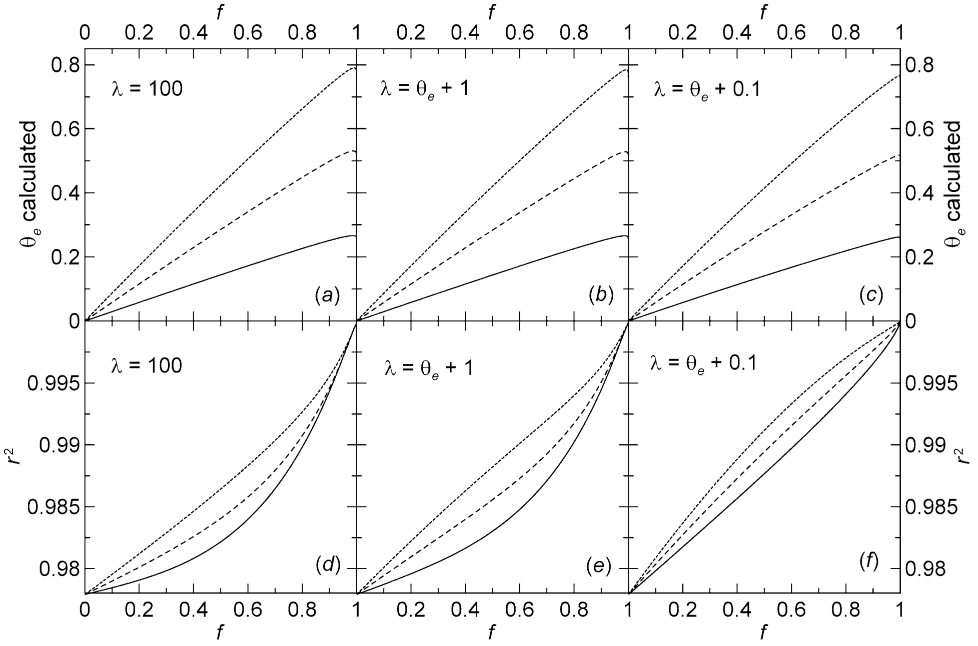

Fig. 7 Approach A. The results of the linear fitting of the pseudo-second order plots generated by using the SRT equation (20) written for the rate of adsorption onto a heterogeneous solid surface ($\alpha = 0.67$). All the other details as in Fig. 6

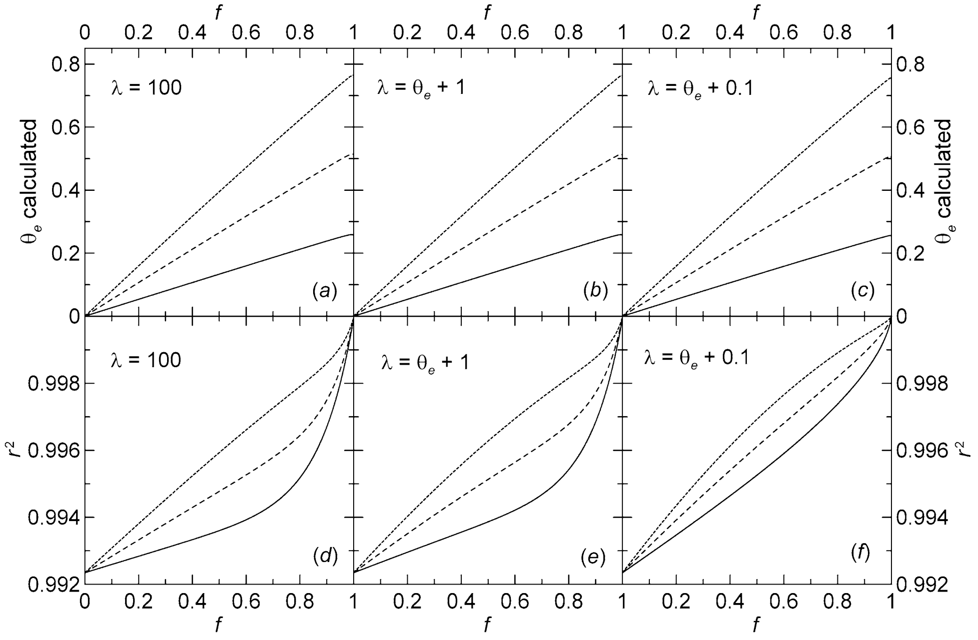

Fig. 8 Approach A. The results of the best-fit procedure of the pseudo-second order plots generated by using the SRT equation (20) written for the rate of adsorption onto a strongly heterogeneous solid surface ($\alpha = 0.33$). All the other details as in Fig. 6

- Introducing heterogeneity improves significantly the linear fits (this observation is consistent with the results presented in Figs. 2 and 4). The same is true for the increasing value of λ parameter (i.e. the decreasing solid/solution ratio in the system).
- The values of the determination coefficients indicate that the quality of the linear fits is satisfactory in all the studied cases (r^2 value is always larger than 0.96) even when the calculated θ_e values are not close to the "real" ones. Thus, the good correlation of data by the pseudo-second order plots does not necessary speak for the accuracy of the θ_e values obtained in this way. Therefore, such a simple fitting procedure cannot be treated as a criterion of applicability or inapplicability of the so-called "pseudo-second order model".

3.2.2 Approach B

The method described in the previous subsection is based on analyzing all the measured experimental (t, θ) points. However, knowing that the pseudo-second order plots estimate θ_e values best when the f value is high, one can propose

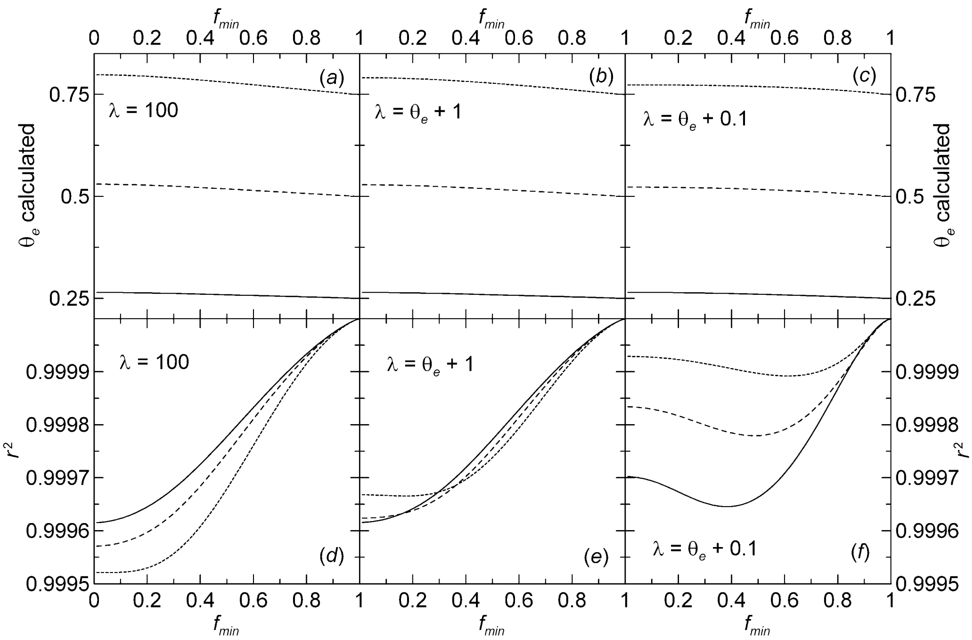

Fig. 9 Approach B. The results of the linear fitting of the pseudo-second order plots generated by using the SRT equation (8) (homogeneous surface). The calculations were performed for three different values of λ parameter, three values of equilibrium surface coverages: $\theta_e = 0.25$ (——), $\theta_e = 0.5$ (– – –) and $\theta_e = 0.75$ (- - - - -) and $f = 0.99$. The changes of calculated θ_e values (i.e. reciprocal of tangent determined from linear regression) are presented in panels (**a**), (**b**) and (**c**) while the corresponding r^2 values are shown in panels (**d**), (**e**) and (**f**)

still another method. Let us consider the situation when the pseudo-second plot is applied for only part of the experimental kinetic data. The findings presented in the previous subsection indicate that the most promising procedure is to apply those parts of kinetic isotherms, which are measured at long times, i.e. when the system is close to equilibrium.

Let us introduce the additional parameter, $f_{\min}$. It can be defined by the following equation:

$$f_{\min} = \frac{\theta(\tau = \tau_{f_{\min}})}{\theta_e}, \qquad (21)$$

where $\tau_{f_{\min}}$ is the time at which the ratio $\theta/\theta_e = f_{\min}$ and $f_{\min} < f$. As in the case of f parameter, the value of $f_{\min}$ defines simultaneously $\tau_{f_{\min}}$. Now the assignment $\tau_{f_{\min}} = 0$ is made so the studied range of times is again $\tau \in (0; 1)$ and the range of surface coverages is $\theta \in (f_{\min}\theta_e; f\theta_e)$. The idea of using both f and $f_{\min}$ coefficients is illustrated symbolically in part (B) of Fig. 1. It can be said that Approach B is based on cutting off some part of kinetic data for which the condition $f_{\min}\theta_e < \theta < f\theta_e$ is not fulfilled.

The other details of our procedure (i.e. generating the pseudo-second order plots using (8) and (20), performing linear regressions for each plot and their results) are identical to those described in the previous subsection. All calculations are performed for $f = 0.99$. The results of our calculations performed for both homogeneous and heterogeneous surfaces are presented in Figs. 9–11.

The following observations can be made:

- The application of Approach B leads generally to correct values of θ_e; deviations are more significant when $f_{\min} \to 0$.
- The obtained values of θ_e are always slightly higher than the actual ones.
- These observations are true for all the values of λ parameter and/or degree of heterogeneity. i.e. the value of α parameter.
- The quality of the obtained fits is extremely high (r^2 value is always larger than 0.9995).
- Introducing heterogeneity additionally improves the goodness of these fits. The increasing value of λ parameter has a similar effect.

3.3 The influence of the experimental error

The influence of experimental errors was studied by using the non-linear form of the pseudo-second order equation (18). The pseudo-experimental error was incorporated by accepting normal (Gaussian) distribution and a certain value of θ_e. The $\theta_{err}(t)$ values, including errors, were calculated for each t value with the mean $\theta(t)$ (calculated from (18)) and the standard deviation $z\theta_e$. We assumed that z can vary from 0 to 0.1. As one can easily check, this range corresponds to the most common situations in the real kinetic experiments. The number of $(t, \theta_{err}(t))$ points was always accepted as equal to 20. During a kinetic experiment one usually obtains data in the form (t, c). The real, experimental errors manifest themselves mainly through the monitored, time-dependent sorbate concentration in the bulk solution. As this concentration, c, is the linear function of surface coverage (see (6)), incorporating errors directly to the θ values seems to be reasonable.

In the next step, we transformed the pseudo-experimental points to the pseudo-second representation, i.e. $(t, \theta) \to$

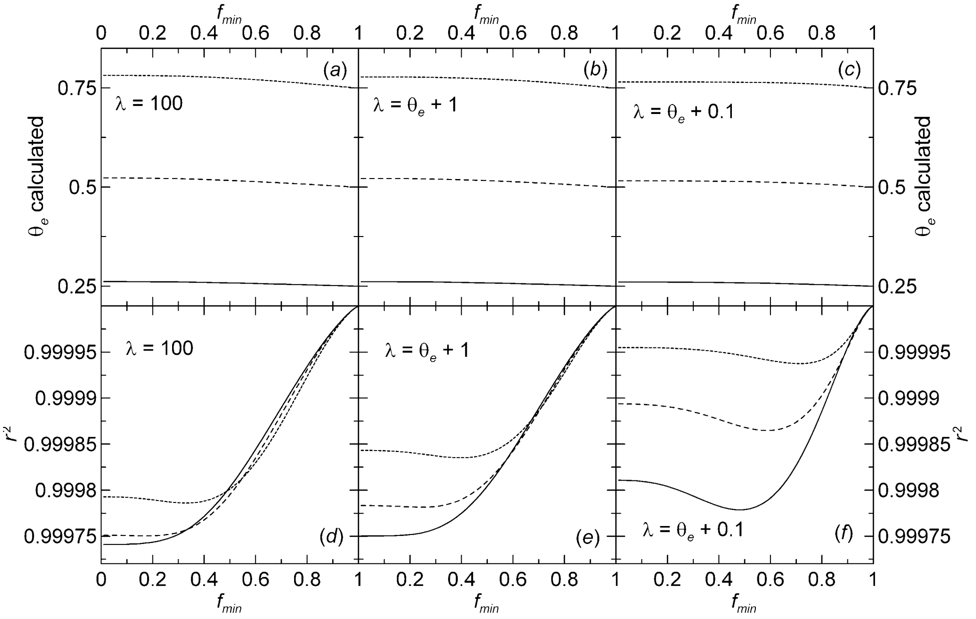

Fig. 10 Approach B. The results of the linear fitting of the pseudo-second order plots generated by using the SRT equation (20) (heterogeneous surface, $\alpha = 0.67$). All the other details as in Fig. 9

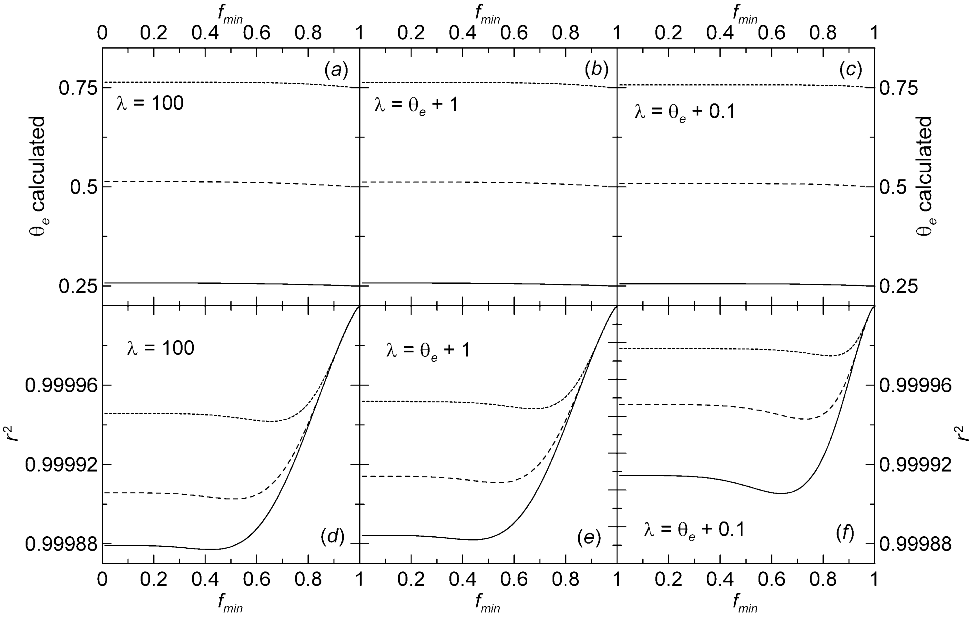

Fig. 11 Approach B. The results of applying the best fit procedure for the pseudo-second order plots generated by using the SRT equation (20) (strongly heterogeneous surface, $\alpha = 0.33$). All the other details as in Fig. 9

$(t, t/\theta(t))$ and a simple linear regression was performed for them. The cases of this regression were as usual, (i) the reciprocal of tangent, i.e. "θ_e calculated" and (ii) the coefficient of determination, r^2. Every result was averaged over 10000 configurations.

It is obvious that this method leads to estimating only the errors inherent in the pseudo-second order linear representation (15). The situations when the pseudo-second order equation is not able to represent the adsorption kinetics in a given system are not considered here, due to the large complexity of such an issue. It is commonly known that applying some simple linear representations may lead to the increasing or the decreasing effect of experimental errors. However, the real experimental errors are inseparably connected with the experimental set-up, applied procedure and with many other important factors. Errors originating from these factors should be considered individually for each considered adsorption system.

The obtained results indicate that the errors inherent in the representation (15) can be safely neglected. Incorporating errors practically does not affect θ_e values calculated from these linear regressions. This observation is valid for the whole possible range of f and θ_e parameters (in both cases this range is identical, i.e. (0; 1)) as well as for the extremely large errors ($z = 0.1$). The maximum deviations (observed for $z = 0.1$) do not exceed 1% of the actual values of θ_e.

4 Conclusions

- Both the popular pseudo-second order and the Elovich equations are essentially identical when considering surface coverages lower than about $0.7\theta_e$. The relations between their coefficients are given in Appendix A.
- The pseudo-second order equation is identical with our "generalized-Elovich" equation (13) up to $0.9\theta_e$. This hypothesis launched in our previous paper (Rudzinski and Plazinski 2006) has been quantitatively proved here.
- The above mentioned conclusions are true for all the values of the equilibrium surface coverage.
- Two methods of determining θ_e values have been tested (Approaches A and B); both based on the general relation (19) and the statistical rate theory represented by either (8) (homogeneous solid surface) or (20) (heterogeneous solid surface). Applying both these methods indicates that the pseudo-second order equation can be very useful for reliable determination of the values of the equilibrium adsorbed amount. The only essential condition is that one has to have at their disposal a significant part of kinetic data measured close to equilibrium.
- Approach A is identical with the commonly applied procedure of correlating the measured kinetic data by using the pseudo-second order linear representation (15). Approach B is based on taking into account only this part of kinetic data which were measured when the system was close to equilibrium.
- Approach B is more precise than Approach A, but the necessary condition to obtain the correct results is that one could have at their disposal experimental points measured very close to equilibrium (in our study the last point was at $\theta = 0.99\theta_e$). However, the same can be stated about the accuracy of Approach A.
- The quality of the linear fits is satisfactory in the case of Approach A (r^2 value is always higher than 0.96) and extremely high in the case of Approach B (r^2 value is always higher than 0.9995).
- The good linear correlation of data by the pseudo-second order plots does not necessarily speak for the accuracy of the θ_e values obtained in this way.
- Increasing both the degree of surface heterogeneity and the solid/solution ratio improves the quality of the pseudo-second order fits as well as the accuracy of θ_e values obtained in this way.
- The influence of the experimental error connected with the pseudo-second order linear representation (15) is not significant for correct determination of the equilibrium surface coverage values, and can be neglected as a rule.

Appendix A

Let us write the Elovich equation in the following form:

$$\frac{d\theta}{dt} = \beta e^{-\gamma\theta}, \tag{22}$$

where $\beta = K'_{ls} e^{\gamma\theta_e}$. For the sake of clarity, let us also represent the kinetic isotherms expressed by the integral forms of the Elovich equation (22) and the pseudo-second order equation (18) as $\theta_{El}(t)$, and $\theta_{PS}(t)$, respectively. Trying to estimate the quality of the fits presented in Fig. 2, one has to define the error function:

$$G(\gamma, \beta, f, \theta_e) = \int_0^1 [\theta_{El}(t) - \theta_{PS}(t)]^2\, dt. \tag{23}$$

Integration in the range $t \in (0; 1)$ is the effect of accepting the time scale for which the adsorbed amount can vary from 0 to $f\theta_e$. When f and θ_e values are accepted, the best-fit parameters γ and β, leading to the best correlation of $\theta_{PS}(t)$ function by $\theta_{El}(t)$ function, can be determined from the following conditions, leading to the minimum of $G(\gamma, \beta)$:

$$\begin{cases} \frac{\partial G(\gamma,\beta)}{\partial \gamma} = 0, \\ \frac{\partial G(\gamma,\beta)}{\partial \beta} = 0. \end{cases} \tag{24}$$

However, the condition (24) does not lead to analytical solutions for γ and β when one applies the $\theta_{El}(t)$ and $\theta_{PS}(t)$ functions defined in (22) and (18), respectively. Nevertheless, one can find compact simple expressions for γ and β by applying the following approximations.

After expanding the right-hand-sides of (22) and (18) into the Taylor series around $t = 0$, one obtains for the case of the Elovich equation:

$$\theta_{El}(t) = \beta t - \frac{1}{2}\gamma\beta^2 t^2 + \frac{1}{3}\gamma^2\beta^3 t^3 - \frac{1}{4}\gamma^3\beta^4 t^4 + \cdots \tag{25}$$

while for the pseudo second-order equation, we have:

$$\theta_{PS}(t) = \frac{f}{1-f}\theta_e t - \left(\frac{f}{1-f}\right)^2 \theta_e t^2 + \left(\frac{f}{1-f}\right)^3 \theta_e t^3 - \left(\frac{f}{1-f}\right)^4 \theta_e t^4 + \cdots. \tag{26}$$

Taking into account only the first two terms for each of these expansions, one obtains the following approximate expression for the error function:

$$G(\gamma, \beta) = \int_0^1 \left[\beta t - \frac{1}{2}\gamma\beta^2 t^2 - \left(\frac{f}{1-f}\theta_e t - \left(\frac{f}{1-f}\right)^2 \theta_e t^2\right)\right]^2 dt. \tag{27}$$

Then, the combination of condition (24) and (27) yields the expressions for γ and β parameters, as functions of the two other parameters, f and θ_e, whose values are to be used to generate the fitted points:

$$\begin{cases} \gamma = \frac{2}{\theta_e}, \\ \beta = \frac{f\theta_e}{1-f}. \end{cases} \tag{28}$$

Of course, the accuracies of the approximation (27) and of the obtained expression for γ and β (28) are the highest in the limits $f \to 0$ and $\theta_e \to 0$ which is due to the general features of the Taylor expansions (25) and (26).

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