Tafel Analysis in Practice

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Abstract

Voltammetric waves under five different mass-transport regimes (macroelectrode, microdisc, micro-hemisphere, micro-hemicylinder and single microband) for an irreversible one-electron transfer process were simulated and analysed to find the appropriate Tafel region for accurate analysis. The transfer coefficient was found to deviate significantly from its true value as a function of potential in all cases due to the influence of mass-transport. If and how a simple analytical mass-transport correction in which the current is corrected for the change in the reactant concentration at the surface can be used to improve the measurement of transfer coefficient was investigated. It is shown that this correction is only rigorously valid for a uniformly accessible microelectrode under a true steady-state condition. This translates to hemispherical electrodes only of the set of five considered. The fraction of the current used in Tafel analysis (Tafel region) can be increased to around 50% for quasi-steady state regimes (hemicylindrical and single band electrodes) with this analytical correction but it completely failed in linear diffusion regimes (macroelectrodes). In the latter case an improved empirical correction is suggested.

1. Introduction

Voltammetric experiments can yield significant thermodynamic and kinetic information[1,2]. However, due to the convolution of the time and energy domains extraction of this data is often non-facile. In many cases measurement of the related physico-chemical parameters may only be fully achieved through simulation of the system. Notwithstanding this, due in part for ease and expediency, it is very common for voltammetric experiments to be analysed using mathematically analytical procedures. Of these analytical methods, Tafel analysis is a cornerstone of the electrochemist's tool box. Tafel analysis of a voltammogram yields a measure of the electrochemical system's transfer coefficient[3,4]. First, under appropriate conditions, the transfer coefficient can provide information regarding the electrochemical mechanism[5]. Classically, Tafel analysis has been used to great effect in the analysis and elucidation of the catalytic activity of various metal surfaces towards the hydrogen evolution reaction[6,7]. Second, for irreversible voltammetry at a macroelectrode (linear diffusion regime) the transfer coefficient needs to be known in order for the species diffusion coefficient to be accurately determined[8].

The transfer coefficient is a dimensionless parameter and describes how the rate of an interfacial oxidation or reduction reaction varies as a function of the applied potential, under the caveat that the concentration of the reactant at the electrode surface is unaltered from its value in bulk solution. The physical interpretation of the transfer coefficient is often dependent upon the assumption of an underlying electrochemical mechanism. Moreover, for electrochemical processes involving the transfer of multiple electrons and/or the formation and breaking of chemical bonds (i.e. processes comprised of multiple sequential elementary steps) the interpretation of the transfer coefficient is not straightforward[9]. However, for a simple and single electron transfer process the transfer coefficient is commonly qualitatively interpreted as a being a measure of the 'position' of the transition state[8], where a transfer coefficient close to unity implies the transition state is 'reactant-like' and similarly a value close to zero implies a 'product-like' transition state for an oxidative process.

The Butler-Volmer equation is a phenomenological description of the rate of an interfacial redox reaction where the reaction rate increases exponentially as a function of the applied potential. In this framework it is commonly assumed that the transfer coefficient is a constant and independent of the applied potential. In contrast Marcus-Hush theory[10–12] provides a microscopic model of an interfacial electron transfer process, here the rate of the reaction is rationalised in terms of the reaction Gibbs energy and a reorganisation energy[13]. The reorganisation energy is related to the energy required to distort the reactant molecule and its solvation shell to those of the product. Commonly, the force constants for the reduced and oxidised species are assumed to be equal (symmetric): this is equivalent to assuming that at low overpotentials that the transfer coefficient has a value of 0.5. However, even for many apparently outer-sphere redox processes the transfer coefficient is found to deviate from 0.5[14]. Relaxation of the assumption of equal force constants, allows (asymmetric) Marcus-Hush theory to be reconciled with the Butler-Volmer equation[15,16]. The latter can be viewed as a good approximation of the former at low overpotentials and the transfer coefficient can be quantitatively interpreted as reflecting the asymmetry in the force constants for the reduced and oxidised species.

For both the symmetric and asymmetric forms of Marcus-Hush theory, these microscopic theories predict a deviation of the reaction rate from exponentially increase at high overpotentials; ultimately the rate becomes independent of the applied potential, becoming mass-transport controlled. The predicted deviation away from exponentially increasing reaction rate may be expressed as a potential dependent transfer coefficient (or equivalently as a 'curved' Tafel slope). The experimental reporting of such curved Tafel slopes and potential dependent transfer coefficients have historically[17,18] played an important role in validating and advancing our physical insight into this class of heterogeneous reactions. However, during the course of a voltammogram the reactant rapidly becomes depleted at the electrode surface and the rate determining step becomes the mass-transport of material to the electrode surface. Consequently, before interpreting an experimental Tafel plot and the associated transfer coefficient it is important to quantify over what range of voltammetric currents can the voltammogram be directly analysed within the Butler-Volmer approach to yield an accurate measure of the transfer coefficient? A further issue is to what extent can the depletion of the reactant be corrected for using analytical approximations? The present paper addresses and answers these two questions.

2. Background theory

2.1 Butler-Volmer (BV) theory

We consider the following one electron transfer oxidative process under different mass-transport geometries:

$$\mathrm{A} \rightleftarrows \mathrm{B} + e^- \qquad Eq.1$$

where the reactant and product in the process are assumed to have equal diffusion coefficients with only reactant present in bulk solution.

Butler-Volmer (BV) theory is experimentally the most commonly used kinetic model[19,20]. According to BV theory, the oxidative and reductive rate constants (k_a, k_c) are functions of the transfer coefficients, the standard rate constant k^0 and the formal potential E_f^0[8]:

$$k_a = k^0 \, exp\left[\alpha_{a,BV}\theta\right] \qquad Eq.2$$

$$k_c = k^0 \, exp\left[-\alpha_{c,BV}\theta\right] \qquad Eq.3$$

where the anodic transfer coefficient $\alpha_{a,BV}$ and the cathodic transfer coefficient $\alpha_{c,BV}$ are between 0 and 1, $\alpha_{a,BV} + \alpha_{c,BV} = 1$, and θ is the dimensionless potential given by:

$$\theta = \frac{F}{RT}\left(E - E_f^0\right) \qquad Eq.4$$

where E is the potential of the working electrode, F is the Faraday constant (96,485 C mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in K. $\alpha_{a,BV}$ and $\alpha_{c,BV}$ are commonly assumed to be independent of potential.

2.2 Tafel analysis

The International Union of Pure and Applied Chemistry (IUPAC) formally defines the anodic and cathodic transfer coefficients as being experimentally determined values and given by[3,4]:

$$\alpha_a = \frac{RT}{F}\left(\frac{dlnj_{a,corr}}{dE}\right) \qquad Eq.5$$

$$\alpha_c = -\frac{RT}{F}\left(\frac{dln\left|j_{c,corr}\right|}{dE}\right) \qquad Eq.6$$

where $j_{a,corr}$ and $j_{c,corr}$ are the anodic and cathodic current densities corrected for any changes in the reactant concentration at the electrode surface with respect to its bulk value. The definitions avoid the need for any knowledge of the overall number of electrons transferred.

If a process is considered to be fully irreversible, for an oxidative process, when the applied potential is sufficiently far from the equilibrium potential E_{eq}, it is possible to neglect the flux contribution from the reduction. Hence, the electrochemical flux can be expressed as:

$$j_a = k_a[A]_0 = k^0 exp\left[\frac{\alpha_a F(E - E_f)}{RT}\right][A]_0 \qquad Eq.7$$

where j_a is the experimentally measured anodic flux density and $[A]_0$ is the concentration of the reactant at the electrode surface, which is typically different from that in bulk solution except close to the 'foot' of the voltammetric wave. Due to the sensitivity of j_a to $[A]_0$, surface depletion of the reactant can and often does lead to a mass-transport limitation of the measured current.

This electrochemical flux can be directly related to the measured current by:

$$I_a = \int F j_a dA \qquad Eq.8$$

where I_a is the anodic current.

By combining Eq.7 and Eq.8, rearranging and assuming the flux is uniform across the electrode surface, we get the expression:

$$\ln|I_a| = \frac{\alpha_a F(E - E_f^0)}{RT} + ln(FAk^0[A]_0) \qquad Eq.9$$

Consequently, if $[A]_0$ does not deviate significantly from its bulk value, a plot of $\ln|I_a|$ versus E yields a straight line with a gradient proportional to α_a. Hence plots of $\ln|I|$ versus E are commonly used to extract the transfer coefficient from voltammetric data and are referred to as 'Tafel plots'. The resulting line of best fit will yield a measure of the transfer coefficient averaged over a range of potentials. However, mirroring the IUPAC recommendations, if the plot is curved, the transfer coefficient can be defined as a function of potential.

Problematically, implementation of Eq 5 and Eq 6 requires precise knowledge of the mass-transport regime to allow the flux to be suitably corrected for deviations in the surface concentration of the reactant. Consequently, for expediency and/or due to the lack of knowledge regarding the nature of the mass-transport regime (in contrast to Eq 5 and Eq 6), the experimentally accessible parameters are:

$$\frac{RT}{F}\frac{dlnI_a}{dE} = \alpha_{a,nc} \qquad Eq.10$$

$$-\frac{RT}{F}\frac{dln|I_c|}{dE} = \alpha_{c,nc} \qquad Eq.11$$

where I_c is the cathodic current, $\alpha_{a,nc}$ and $\alpha_{c,nc}$ are the non-mass-transport corrected or 'apparent' transfer coefficients. The transfer coefficient α_{nc} may deviate from its true value α_a due to the local depletion of reagents at the electrochemical interface. However, at low current densities (i.e. $I \to 0$), $\alpha_{nc} \to \alpha$.

It is useful to comment that Tafel plots ($\ln|I|$ versus E) as used in this paper differ from its historical form (overpotential η versus $log_{10}I$) as measured from galvanostatic experiments. The classically defined Tafel slope with the unit as mV per decade of current is directly related to the transfer coefficient ($Tafel\ slope = 2.3RT/\alpha_a F$). For example, α_a=0.5 is equivalent to the Tafel slope of ca. 118 mV per decade. In this paper, potentiostatic control is assumed, and consequently it is appropriate to define the Tafel plot as $\ln|I|$ versus E, the slope of which is proportional to the transfer coefficient.

2.3 Mass-transport corrected Tafel analysis

Correction of the current or flux to account for the change in the reactant concentration at the surface requires knowledge of the mass-transport regime. Such corrections may be achieved through numerical simulation using the experimentally measured current as a boundary condition[2]. However, it is far more common to use an analytical expression to provide an approximate mass-transport correction[8,21,22].

The analytical expression is based on the assumption of a uniformly accessible microelectrode, where a true steady state can be attained after sufficient long time. Under these conditions, for a fully irreversible electrode process, the flux can be expressed via the Nernst diffusion layer approximation, where the diffusion layer thickness δ is often taken as invariant with time[8,23] and is:

$$j_a = D\left(\frac{[A]_0 - [A]_{bulk}}{\delta}\right) \qquad Eq.12$$

Under BV theory, the analytical expressions describing mass-transport corrected transfer coefficients α' are:

$$-\frac{RT}{F}\frac{dln\left(\frac{1}{I_a} - \frac{1}{I_{lim}}\right)}{dE} = \alpha_a{}' \qquad Eq.13$$

$$\frac{RT}{F}\frac{dln\left|\frac{1}{I_c} - \frac{1}{I_{lim}}\right|}{dE} = \alpha_c{}' \qquad Eq.14$$

where I_{lim} is the mass-transport limiting current and $\alpha_a{}'$ and $\alpha_c{}'$ are the measured analytically mass-transport corrected anodic and cathodic transfer coefficients, respectively. The full deviation of these expressions is presented in the SI Section 1.

Ideally, α' should have the same value as α after mass-transport correction. However, this analytical mass-transport correction as a result of the breakdown of the assumptions made in its derivation is

not applicable in all cases. Therefore, α' is considered as an analytical *approximation* to the mass-transport corrected transfer coefficient. A linear relationship of $\ln\left|\frac{1}{I}-\frac{1}{I_{lim}}\right|$ with the dimensionless potential θ is expected when the assumptions are met[24]. In this paper, the extent to which how accurate the analytically mass-transport corrected Tafel analysis is under different diffusion geometries is studied.

3. Numerical simulation procedures

The commercially available simulation software DigiSim® is used to simulate the one-dimensional (1D) diffusion models. It is based on a fully implicit finite difference (IFD) algorithm suggested by Manfred Rudolph[25–27] and it allows simulations for a wide range of mechanisms.

The voltammetric response on a 2D diffusion microdisc electrode is simulated using a home-written programme as described elsewhere[28]. It is based on the conformal mapping of the spatial coordinates and uses an exponentially expanding time grid.

Although the current at a microband electrode is often approximated by a hemicylinder of equivalent area ($r = w/\pi$, where r is the radius of the hemicylinder and w is the width of the band), there is no true equivalence between these two geometries[29]. Consequently, a bespoke programme for single microband simulation was written. The geometry of the microband electrode is shown in Figure 1 (a). As the length of the microband is assumed to be macroscale, the diffusion in the y dimension can be regarded constant and only the coordinates *x* and *z* are considered in the simulation. The two-dimensional simulation model is shown in Figure 1 (b). The concentration distribution of the reactant as a function of time and space is calculated via solving the diffusion equation coupled with boundary conditions as shown in Figure 1 (b). In this work, dimensionless parameters are applied. The transformation between the dimensional and dimensionless parameters is listed in Table 1. The diffusion coefficients of the redox couples are assumed to be the same and initially there is only the reactant in bulk solution. The boundary condition at the microband electrode is the BV equation and can be written as:

$$\frac{\partial C}{\partial Z} = K^0 exp(\alpha_a \theta)C - K^0 exp(-\alpha_c \theta)(1-C) \qquad Eq.15$$

where $\alpha_a + \alpha_c = 1$[3,4]. K^0 is the dimensionless format of the standard electrochemical rate constant. The dimensionless overpotential θ is the difference between the applied potential on the electrode and the formal potential of the redox reaction. To simulate the cyclic voltammetry, the applied potential is defined as a function of the scan rate as:

$$\theta = \begin{cases} \theta_i + \sigma\tau & \tau \le \frac{\theta_r - \theta_i}{\sigma} \\ \theta_r - \sigma\left(\tau - \frac{\theta_r - \theta_i}{\sigma}\right) & \tau > \frac{\theta_r - \theta_i}{\sigma} \end{cases} \qquad Eq.16$$

[θ_i θ_f] is the potential window in the cyclic voltammetry. For the oxidative reaction discussed in this work, $\theta_i < \theta_f$. The current *J* measured on the microband electrode is calculated from the concentration gradient on the electrode surface:

$$J = 2\int_0^1 \frac{\partial C}{\partial Z} dX \qquad Eq.17$$

The theoretical model is numerically solved by the finite difference method and the alternating direction implicit (ADI) method[30]. The simulation program is written in Matlab R2017a and run on an Intel(R) Xeon(R) 3.60G CPU.

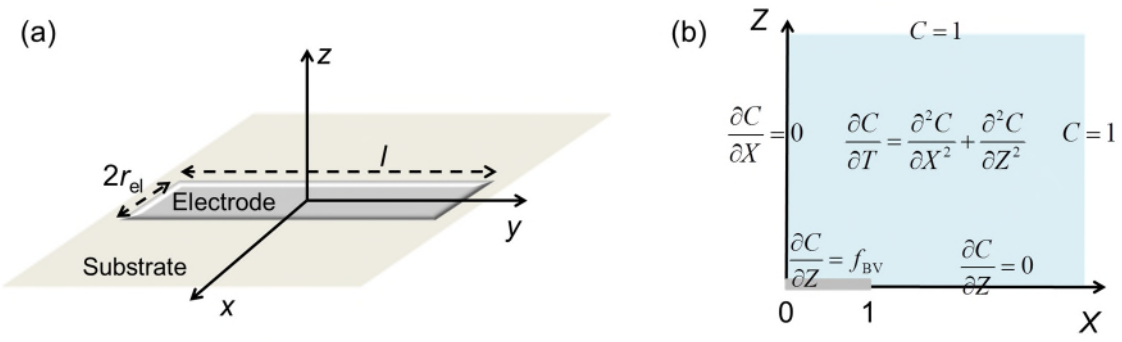

Figure 1 (a) A microband electrode in the Cartesian coordinate. (b) The simulation model for the redox reaction on the microband electrode. f_{BV} is the Butler-Volmer equation as written in Eq.15.

Table 1 Interpretation and transformation of dimensionless parameters.

SI unit parameters	Interpretation	Dimensionless parameters
r_{el} (m)	Half of the electrode width (microband); Radius of the electrode (disc, sphere, cylinder)	$R_{el} = r_{el}/r_{el} = 1$
l_{el} (m)	Length of the microband	
x (m)	Space coordinate, parallel to the electrode surface	$X = x/r_{el}$
z (m)	Space coordinate, perpendicular to the electrode surface	$Z = z/r_{el}$
c_{bulk} (mM)	Concentration in the bulk solution	$C_{bulk} = c_{bulk}/c_{bulk} = 1$
c (mM)	Concentration	$C = c/c_{bulk}$
D (m^2 s^{-1})	Diffusion coefficient	$d = D/D = 1$
t (s)	Reaction time	$\tau = t^*D/r_{el}^2$
F (C mol^{-1})	Faraday constant (96485 C mol^{-1})	
R ($J \cdot mol^{-1} \cdot K^{-1}$)	Gas constant (8.3145 $J \cdot mol^{-1} \cdot K^{-1}$)	
T (K)	Experiment temperature (298.2 K)	
E_f (V)	Formal potential	
E (V)	Applied electrode potential	$\theta = (E - E_f)F/(RT)$
k^0 (m s^{-1})	Standard electrochemical rate constant	$K = k^0 r_{el}/D$

***v* (V s^{-1})**	Scan rate	$\sigma = vFr_{el}^2/(RTD)$
***I* (A)**	Current	$J = I/(FDc_{bulk}l_{el})$

4. Results and discussion

Oxidative voltammograms on different electrode geometries were simulated. The waveshapes and the non-mass-transport corrected ('apparent') transfer coefficient α_{nc} as a function of potential were analysed. We first aim to assess over which range of voltammetric current without mass-transport correction α_{nc} closely reflects the true transfer coefficient α. Second, the accuracy or otherwise of using the analytical defined mass-transport correction (Eq 13 and Eq 14) is investigated.

The process studied in this paper is a fully irreversible, one-electron transfer reaction (Eq 1). Five different diffusion geometries, linear, hemisphere, microdisc, hemicylinder and single band, are investigated in this work. Voltammograms on different geometries were simulated using either DigiSim® or a home-written programme. The analysis presented here focuses on oxidative processes only, but the results are also equally applicable to the irreversible reductive processes. Both the anodic and cathodic transfer coefficients as used in the BV equation are a given value of 0.5 except where otherwise stated. All the Tafel analysis was undertaken in the current range from 1% to 99% of the peak current I_{peak} or steady-state current $I_{s.s}$. Experimentally, the lower limit percentage of current should be chosen based on the ratio of faradaic current to background current, this lower limit will vary between different electrode systems, further details on which are outlined in the discussion presented in the SI Section 2. Three mass-transport regimes will be discussed in the sequence: linear diffusion, steady-state and quasi-steady state.

4.1 Electrodes with linear diffusion

4.1.1 *Tafel analysis under linear diffusion*

For a planar disc electrode, both linear and radial (near the electrode edge) diffusion contribute to the total mass-transport limited flux. However, at sufficiently short times or for larger electrodes, when the diffusion layer thickness is small as compared to the electrode radius, only the linear diffusion contribution needs to be considered. The limits of this linear diffusion regime can be described via the dimensionless scan rate σ (Defined in Table 1). When σ is >3350[31] – as is commonly encountered when using a macroelectrode – the diffusion to the electrode can be assumed to be linear. Under these conditions the resulting maximum current is expected to be within experimental error (no more than 3% greater compared to that predicted for a linear diffusion regime from Randles-Ševčík equation)[31]. The flux is then considered as uniform over the electrode surface and results in a peak-shaped cyclic voltammogram (Figure 2(a)).

Voltammograms on linear diffusion electrodes at different dimensionless scan rates were simulated using DigiSim®, with the transfer coefficients α_a and α_c equal to 0.5 and a dimensionless rate constant K of 1.5×10^{-3}. In the fully irreversible limit, although the magnitude of the peak current is proportional to the square root of the scan rate and its position on the potential scale shifts with the scan rate, the dimensionless voltammetric *waveshape* is independent of the dimensionless scan rate. The details are presented in SI Figure 1. The voltammogram simulated for a dimensionless scan rate

of 2.19×10^4 was selected for Tafel analysis. Figure 2(a) shows the voltammogram normalised relative to the voltammetric peak current. The Tafel plot ($\ln|I_a|$ versus θ) was then calculated over the current range of 1% to 99% of the peak current and is shown in the inlay of Figure 2(a). The slope of the Tafel plot corresponds to the anodic transfer coefficient $\alpha_{a,nc}$. It can be seen that the Tafel plot is not a straight line over the potential range; the value of $\alpha_{a,nc}$ is not a constant.

In order to more clearly visualise how the non-mass-transport-corrected anodic transfer coefficient changes with dimensionless potential θ, the first derivative of the Tafel plot (Eq 10) is presented as the blue curve in Fig 2(b). It shows that at very low current, the measured anodic transfer coefficient $\alpha_{a,nc}$ approaches the true value of 0.5, but deviates from this value at high currents. This deviation occurs due to the depletion of the reactant at the electrode surface. Upon reaching the peak current the 'apparent' or non-mass-transport corrected transfer coefficient ($\alpha_{a,nc}$) tends to zero. Moreover, in order to numerically express how far the measured $\alpha_{a,nc}$ deviates from the true value as a function of potential, the fraction of the oxidative wave that can be used in the Tafel analysis for a given error has been calculated using Eq 18. The results are tabulated in the first line in Table 2.

$$Error\ in\ \alpha_a = \frac{|measured\ transfer\ coefficient\ \alpha_{a,nc} - true\ transfer\ coefficient\ \alpha_a|}{true\ transfer\ coefficient\ \alpha_a} \times 100\% \qquad Eq.18$$

Frequently, up to 50% of the rising part of the voltammogram is taken for Tafel analysis in order to get rid of the influence from background current and diffusion effect[8,32]. However, from the results presented in Table 2 it can be seen that at 50% of the way up the voltammetric wave the value of the measured transfer coefficient is significantly below its actual value.

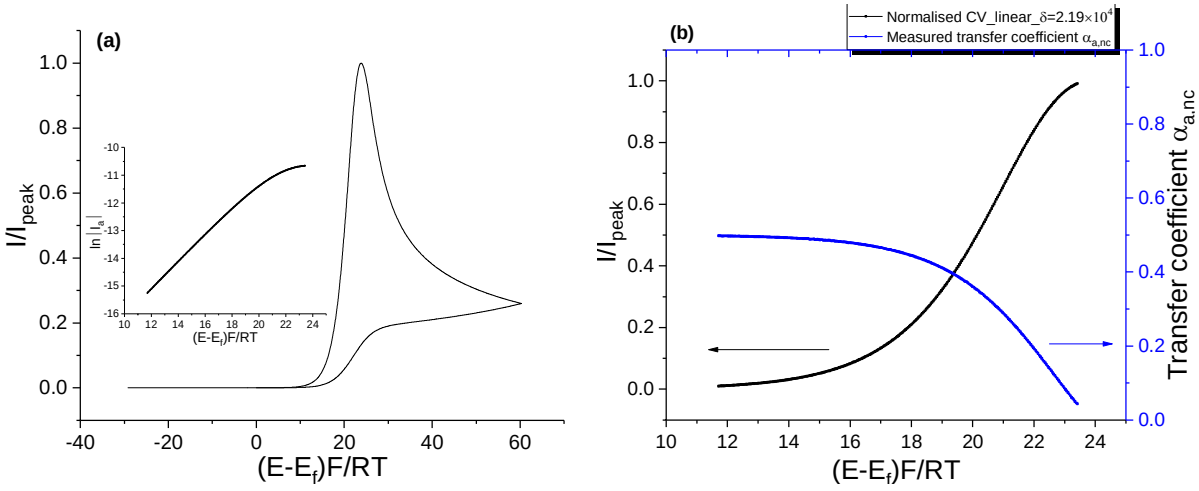

Figure 2 (a) Effect of various dimensionless scan rates on the wave-shape of linear diffusion at a dimensionless scan rate of 2.19×10^4. The inlayer is the Tafel plot in the current of 1% to 99% of the peak current. (b) Measured anodic transfer coefficient plot for linear diffusion in the current of 1% to 99% of the peak current (Black: oxidative wave; blue: measured transfer coefficient). The dimensionless rate constant $K=1.5\times10^{-3}$. Transfer coefficients assumed in the simulation: $\alpha_a = \alpha_c = 0.5$.