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## DYNAMIC MODELS OF ION-SELECTIVE ELECTRODES WITH THEIR ELECTRONIC INTERFACE

Dynamic models of an ion-selective electrode are analysed in this article taking into account the independence of values of its dynamic parameters from the value and direction of activity change. Unfortunately, a complicated mathematical representation of a new model makes the model difficult to be applied in practice. Therefore, some simplifications are made constructing two semi-empirical models: 1) a model with the  $k$  parameter and 2) a model basing on two other models well-known from the literature. Verifications of the new models have been performed using the measuring set-up built in the Division of Measurement Systems at the Silesian University of Technology. Obtained results proved that the model with the  $k$  parameter completely fulfils the goal of the article – its dynamic parameters are dependent on the slightest degree of the kind of activity step.

Keywords: potentiometry, ion-selective electrode, dynamic models

### 1. DYNAMIC PARAMETERS OF ION-SELECTIVE ELECTRODES

Ion-selective electrodes (ISEs) belong to the group of electrochemical sensors with the help of which it is possible to determine the quantitative and qualitative contents of a solution. One of the main electrode features is its response time toward a change of ion activity in a sample. Many determinants impact on the total response time by the influence on physical and chemical phenomena taking part in the response process. They can be: the type and construction of the electrode, its working mechanism, sample flux through the cell and response time of the electric circuit [1]. The response time is especially important in research into kinetics of chemical reactions and into *in-vivo* measurements as well as in monitoring of water and sewage contents, where the concentration of ions is very low.

All of known dynamic models describing the response of the electrode toward the ion activity step are simplified by omitting less significant phenomena which appear in the response process. The basis of contemporary models is usually one arbitrarily chosen phenomenon which determines, according to its authors, the slowest stage in the response process. This stage is known as Rate-Limiting-Step (RLS). These models base on the existence of a) an energetic barrier on the sample / membrane phase boundary, b) a chemical reaction, c) diffusion in the unstirred boundary layer. Empirical and semi-empirical models are also described in the literature. Those dynamic models that are frequently used to approximate the real dynamic responses of ion-selective electrodes are collected in Tab. 1 [2].

The dynamic parameter  $T$  can be defined in various ways (*cf.* Tab. 1). Therefore some other parameter is frequently used. It is the practical response time  $t_{90}$ . It is defined as the time after the change of ion activity in the sample needed to achieve 90% of its steady-state value [10]. The parameter is, due to its simplicity, very often given by the producers as a response time of ISE.

This article is an attempt to elaborate a new dynamic model, the parameters of which are almost independent of the value and direction of activity change.

Table 1. Selected dynamic models of ion-selective electrodes

Model's author	RLS	Mathematical representation
Rechnitz-Hameka [3]	Energetic barrier on the sample   membrane phase boundary	$E(t) = E_1 + (E_2 - E_1) \left( 1 - e^{-\frac{t}{T}} \right)$ (1)
Tóth-Pungor [4,5]	Kinetics of chemical reaction near or on the membrane surface	$E(t) = E_2 + S \lg \left[ 1 - \left( 1 - \frac{a_1}{a_2} \right) e^{-\frac{t}{T}} \right]$ (2)
Lindner <i>et al.</i> [6,7,8]	Diffusion through the boundary layer	$E(t) = E_1 + S \lg \left[ 1 + \left( \frac{a_2}{a_1} - 1 \right) \left( 1 - e^{-\frac{t}{T}} \right) \right]$ (3)
Shatkey [9]	Empirical model	$E(t) = E_1 + (E_2 - E_1) \frac{\frac{t}{T}}{1 + \frac{t}{T}}$ (4)

$E(t)$  – step response of ISE in V;  $E_1, E_2$  – initial and steady-state value of the response in V, respectively;  $S$  – Nernstian slope of ISE in V;  $a_1, a_2$  – initial and final ion activity, dimensionless, respectively;  $T$  – dynamic parameter in s,  $t$  – time in s,  $\lg(\cdot)$  – common logarithm.

## 2. NEW DYNAMIC MODEL

A primary assumption which is a cornerstone of the elaborated model, is the fact that it is necessary to take into consideration two phenomena. The first phenomenon is a physico-chemical one. It takes place in the boundary area between the solution and electrode's membrane. A change in the ion activity transforms to a change in the electrode potential according to the Nernst equation [11].

The second phenomenon, significantly influencing the electrode's potential in its transient-state, is related to the time constant of the electronic circuit's input. An electrochemical cell containing the measuring electrode, the sample and reference electrode, is a voltage source with very high output impedance. Because of the existence of connecting wires and of the input circuit of the voltage meter, the cell with these elements forms a RC circuit. The value of its time constant can be even comparable to or greater than the value of the response time of the chemical part [12].

The working mechanism of the whole measurement system can be illustrated in Fig. 1.

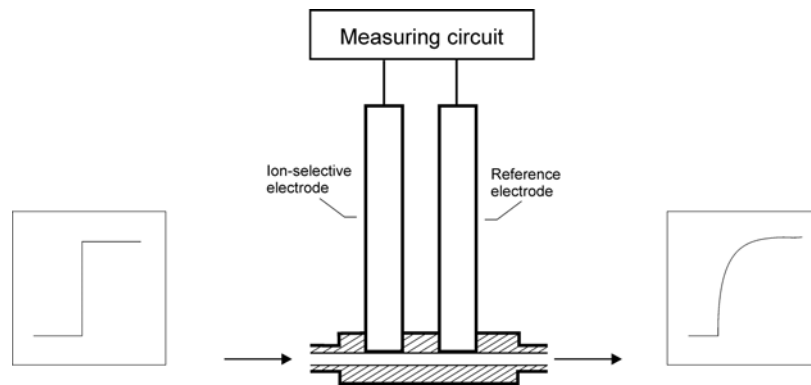


Fig. 1. Diagram of measuring set-up with an ion-selective electrode.

The measuring system is represented as a block diagram in Fig. 2:

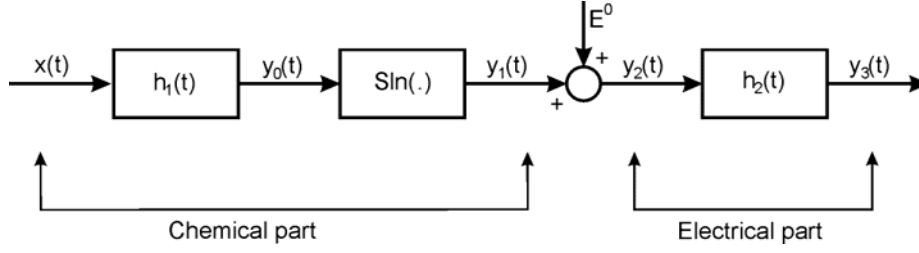


Fig. 2. Block diagram of the electrochemical measuring cell.

where:

- $x(t)$  – step change in ion activity;
- $y_0(t)$  – response of the chemical part taking into account its inertia;
- $y_1(t), y_2(t)$  – response of non-inert non-linear system to signal  $y_0(t)$  (corresponding to the Nernst equation);
- $y_3(t)$  – response of the whole ISE, taking into account additional inertia in the electronic part;
- $h_1(t), h_2(t)$  – response of the chemical and electronic part, respectively, to a Dirac impulse  $\delta(t)$ .

Assumptions:

- The system is in the steady-state for time  $t < 0$ . Ion activity near the electrode is  $a_1$ . Electrode's potential is  $E_1$ .
- The step change in ion activity from  $a_1$  to  $a_2$  is at the time  $t = 0$ .
- The system achieves the steady-state for  $t \gg 0$ . Electrode's potential is  $E_2$ .

It is assumed that  $h_1(t)$  and  $h_2(t)$  are unit impulse responses of the first-order inertia. Therefore, impulse responses of the chemical and electronic parts are [13]:

$$h_1(t) = \frac{1}{T_{ch}} e^{-\frac{t}{T_{ch}}} u(t), \quad h_2(t) = \frac{1}{T_{el}} e^{-\frac{t}{T_{el}}} u(t), \quad (5)$$

where  $u(t)$  is the symbol of a unit (Heaviside) step function. The step change in activity  $x(t)$  follows, according to:

$$x(t) = a_1 + \Delta a u(t). \quad (6)$$

Because the value of activity change can be large, the use of linearization or Laplace transformation is impossible. Therefore, a convolution of functions is applied. To solve the integral function, the logarithm is expanded in a Taylor series. Calculations are very complex and are omitted in the work. As a result, the following relationship is obtained:

$$E(t) = E^0 + S \ln(a_1) u(-t) + S \left[ \ln(a_1) e^{-\frac{t}{T_{el}}} + \ln(a_2) \left( 1 - e^{-\frac{t}{T_{el}}} \right) - \sum_{n=1}^{\infty} \left( \frac{\Delta a}{a_2} \right)^n \frac{1}{1 - \frac{nT_{el}}{T_{ch}}} \frac{1}{n} \left( e^{-\frac{nt}{T_{el}}} - e^{-\frac{t}{T_{ch}}} \right) \right] u(t). \quad (7)$$

### 3. SIMPLIFICATIONS OF THE DYNAMIC MODEL

Such a complicated mathematical representation of the model (7) leads to numerical errors during calculations even if a 96-bit floating-point arithmetic is applied. The value calculations of the model take significant time and may need a very long time during approximation of experimental data. Therefore, simplification of the model is required. The task is very difficult when mathematical transformations are used. However, using a semi-empirical approach make it possible.

Model (7) bases on the assumption that the response rate of ISE is dependent on two first-order inertias. The linear part of the model describes the phenomena that are also linear (mainly inertia of the electronic measurement system). The logarithmic part describes non-linear phenomena (mainly ion diffusion into the membrane surface). The assumption is also valid for derivations of the simplified model.

### 3.1. Model with the $k$ parameter.

A dynamic model with the  $k$  parameter is the first simplification of the model (7). It is constructed by a simple interconnection of two first-order inertias:

- linear first-order inertia, which models electrical phenomena on the sample / membrane phase boundary and in the electric circuit:

$$y_{el}(t) = 1 - e^{-\frac{t}{T_{el}}}, \quad (8)$$

- linear first-order inertia, which models phenomena in the chemical part of the measurement circuit:

$$y_{ch}(t) = 1 - e^{-\frac{t}{T_{ch}}}. \quad (9)$$

Interconnection of the two inertias (8) and (9) using a non-linear equation describing static processes, gives a dynamic model, which takes into considerations phenomena taking place in both the chemical and electronic part of the measurement system:

$$E(t) = E_1 + (E_2 - E_1) \left( 1 - e^{-\frac{t}{T_{el}}} \right) \lg \left[ k + (10 - k) \left( 1 - e^{-\frac{t}{T_{ch}}} \right) \right]. \quad (10)$$

Analyzing the boundary conditions:

if  $t \rightarrow 0$  then  $E(t) = E_1$  and if  $t \rightarrow \infty$  then  $E(t) = E_2$ .

The  $k$  parameter is added into equation in order to avoid indeterminacy of logarithm at time  $t = 0$ . Its physical interpretation is difficult but it can be noticed that its value determines the behaviour of the chemical part. In the range of the parameter from 1 to 10, the more it increases, the smaller the observed influence of the chemical part on the response. Exemplary responses of model (10) are presented in Fig. 3. During approximations, the parameter's value is chosen in the same way as the values of parameters  $T_{ch}$  and  $T_{el}$ . Work on theoretical interpretation of the parameter are going on.

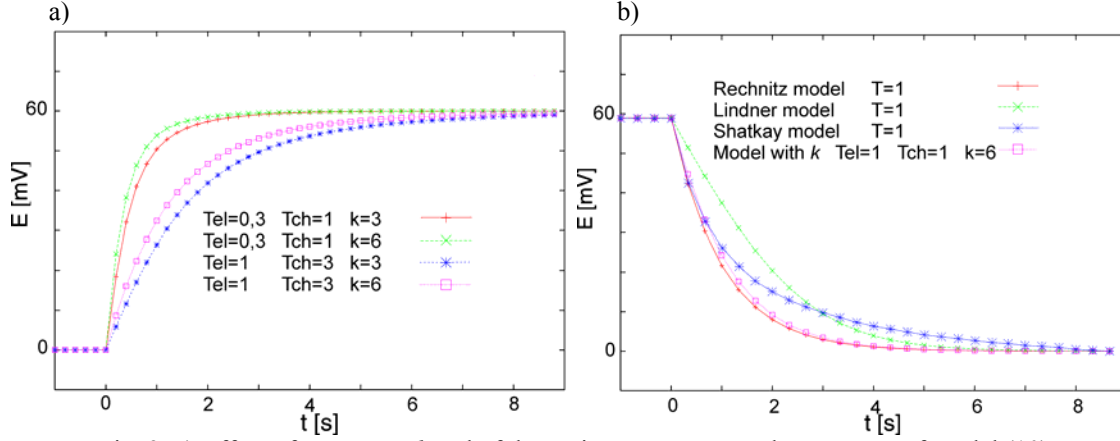


Fig. 3. a) Effect of parameter  $k$  and of dynamic parameters on the response of model (10):  
b) Comparison of model (10) with other models known from literature sources.

### 3.2. Rechnitz-Lindner Model

The next model is a result of interconnection of the two well-known models conducted in the same way as in Sec. 3.1. The models are: 1) the Rechnitz-Hameka model derived by choosing the phenomenon of the existing energetic barrier on the sample/membrane phase boundary as the most important and 2) the Lindner model derived from an analysis of diffusion of ions through the boundary layer:

- Rechnitz-Hameka model:

$$E(t) = E_1 + (E_2 - E_1) \left( 1 - e^{-\frac{t}{T_{el}}} \right), \quad (11)$$

- Lindner model:

$$E(t) = E_1 + S \lg \left[ 1 + \left( \frac{a_2}{a_1} - 1 \right) \left( 1 - e^{-\frac{t}{T_{ch}}} \right) \right]. \quad (12)$$

Interconnection of (11) with (12) gives the following simplification of model (7):

$$E(t) = E_1 + S \left( 1 - e^{-\frac{t}{T_{el}}} \right) \lg \left[ 1 + \left( \frac{a_2}{a_1} - 1 \right) \left( 1 - e^{-\frac{t}{T_{ch}}} \right) \right]. \quad (13)$$

Analysing the boundary conditions:

if  $t \rightarrow 0$  then  $E(t) = E_1$  and if  $t \rightarrow \infty$  then  $E(t) = E_0$ .

Response comparisons of model (13) with Rechnitz-Hameka and Lindner model, as well as responses of model (13) dependent on the value of the dynamic parameter are presented in Fig. 4. The responses are significantly different for the same values of dynamic parameters when different models are applied. Effect of  $T_{el}$  and  $T_{ch}$  on the response is also significantly different using model (13).

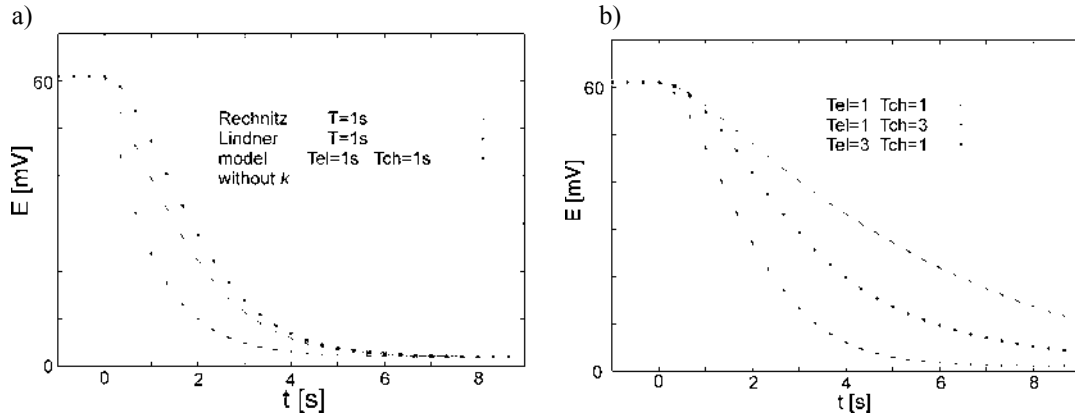


Fig. 4. a) Comparison of the Rechnitz-Hameka model, Lindner model and model (13):  
b) Effect of dynamic parameters on response of model (13).

#### 4. DESCRIPTION OF THE MEASURING SET-UP

The measuring set-up contains three elements (Fig. 5): a flow-cell with measuring electrodes (1), a data acquisition system (2) and a PC computer (3).

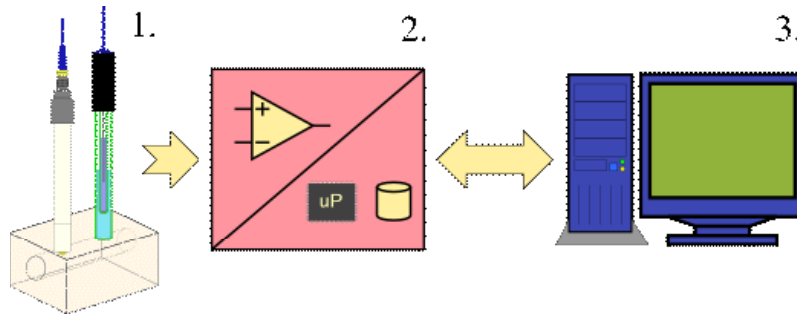


Fig. 5. Block diagram of the measuring set-up.

The flow-cell consists of two blocks made from Plexiglas. The first one is block **A** of the measuring duct, the second one is block **B** consisting of a valve. Two electrodes (diameter 12 mm) are mounted into block **A** forming a measuring cell. A duct (diameter 5 mm) has been drilled through the block. The block is made in such a way that only electrode membranes are placed in the duct.

The block **B** has three ducts: two inlets and one outlet. All of the ducts are placed coplanar. The movable part of the block (frustum of a cone) perfectly fits the whole of the immovable part. Two parallel ducts are drilled in the cone. The choice of the inlet is done by a rotation of the movable part.

A photograph of the flow-cell is shown in Fig. 6. Two electrodes are shown there, which are fastened using special screws. In the front two diodes of the optical sensor are visible. On the right side is block **B** with a handle of the movable part. The electrical circuit is built of: 1) a signal conditioner – impedance converter, an anti-aliasing filter and a temperature-to-voltage converter: 2) a 16-bit A/D converter with analogue multiplexer: 3) digital elements – a microprocessor, a parallel communication interface: 4) power supply adapters – +15V, –15V and +5V. The DAS, while working in the dynamic mode allows to measure four voltages with a frequency in the range of 1 Hz to 5 kHz at each of the inputs and to transmit the results from the DAS to the PC. The assessed standard uncertainty of voltage measurement is 0.4 mV [14].

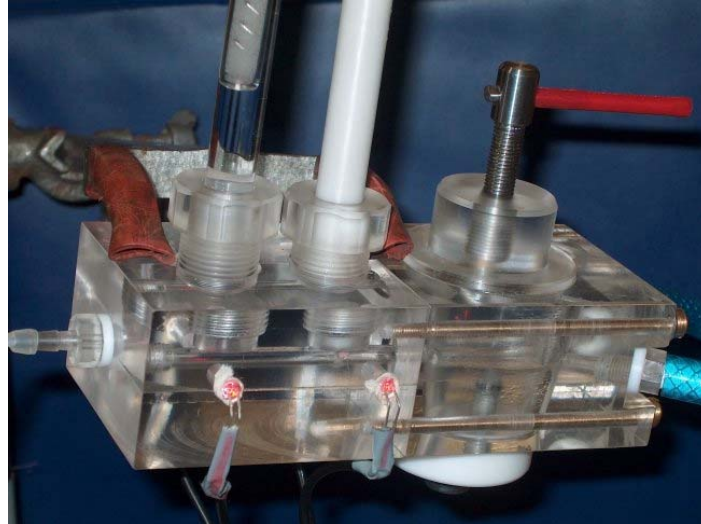


Fig. 6. A photo of the flow-cell dedicated to the research on dynamics of ISEs.

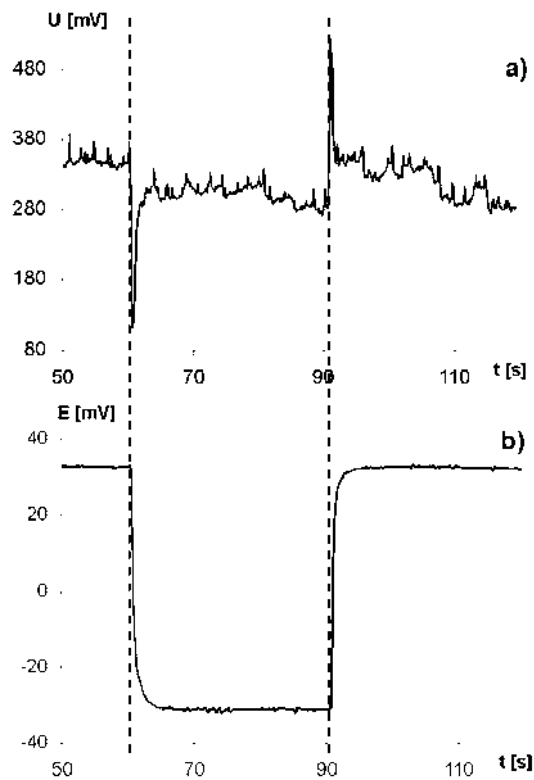


Fig. 7. Dynamic response of a) the optical sensor: b) an ion-selective electrode.

During determination of the dynamic characteristics, the voltage value at one point is usually the mean of 100 measurements performed with a frequency of 1 kHz.

The optical sensor is built of two pairs of LEDs. The measurement of the flow is realized by dyeing one of the samples flowing into the flow-cell's inlet. Analysis of the response registered by the DAS makes it possible to identify the time of the change in solution colour at the point of placing the LEDs and to determine the flow rate.

The set-up contains also a PC computer. It is dedicated to reading the data from the DAS and storing it on a disk.

An exemplary dynamic response of the optical sensor and ISE obtained from the measuring set-up is presented in Fig. 7. It is clearly visible that utilizing of the optical sensor allows one to determine a starting point of the response.

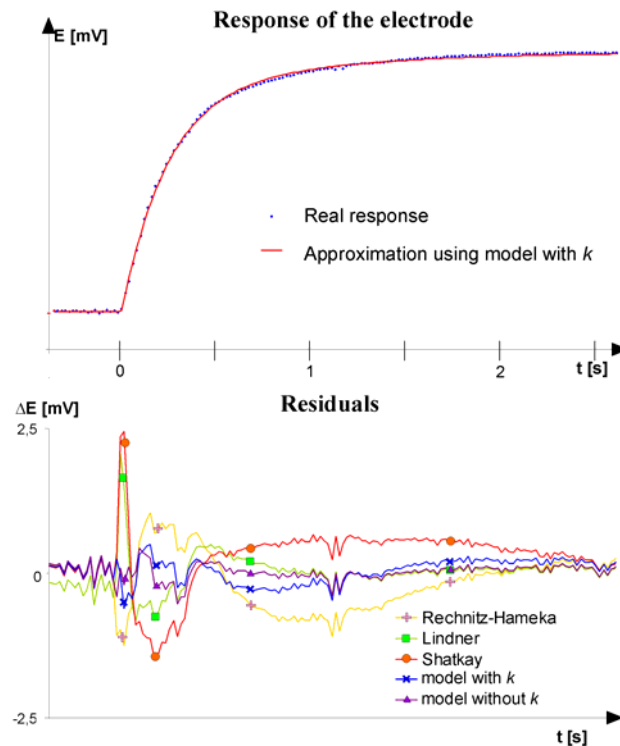


Fig. 8. An approximation of a real dynamic response of measuring electrode obtained using of model (10) and its residuals and residuals of other models.

## 5. VERIFICATION OF THE DYNAMIC MODELS

Verification of the dynamic models has been performed on the measuring set-up. The potassium and sodium PVC ISEs and a silver-chloride reference electrode have been used. The estimations of parameter values have been done using *Solver* add-one to the *Microsoft Excel v.98* spreadsheet [15]. The standard deviation of residuals  $s$  has been chosen as a quality coefficient.

For simplification, the presented models do not have terms with a delay time. The approximations are made taking into account  $t = t' - t_0$ , where  $t'$  is the real time and  $t_0$  is delay time.

An exemplary real dynamic response of ISE with its approximation made using model (10) and model (13) is presented in Fig. 8. Below the approximation charts, residual charts for some models are placed. Exemplary dynamic parameters of these models are collected in Tables 2 and 3.

Models (10) and (13) better fit the real dynamic response than other literature models. The value of dynamic parameters of literature models and  $t_{90}$  depend on the value and direction of activity change in a sample. It is clearly visible in Table 2 where the values in case of an increase and decrease in activity change are compared. Parameter values of model (13) also depend on the direction of activity change. The best results are obtained using model (10) – its values are almost constant for a given electrode.



Table 2. Value comparison of  $t_{90}$  and dynamic parameters of the following models: Rechnitz-Hameka (ReHa), Lindner (Lind), Shatkay (Shat), model (10) (with  $k$ ) and model (13) (without  $k$ ) for the potassium ISE. The  $s$  is the quality coefficient.

MODEL	ReHa	Lind	Shat	with $k$	without $k$	$t_{90}$
PARAMETER	<b>One decade increase in activity in upper measuring range</b>					
T [s]	0.16	0.09	0.06	0.11; 0.97	0.09; 0.58	0.22
$k$ [1]				7.30		
$s$ [mV]	0.99	1.02	0.90	0.75	0.75	
PARAMETER	<b>One decade increase in activity in lower measuring range</b>					
T [s]	0.09	0.10	0.02	0.10; 1.16	0.07; 0.57	0.24
$k$ [1]				8.24		
$s$ [mV]	1.53	1.70	1.87	0.26	0.31	
PARAMETER	<b>Two decades increase in activity</b>					
T [s]	0.11	0.21	0.04	0.10; 1.28	0.08; 0.42	0,30
$k$ [1]				8.90		
$s$ [mV]	0.85	1.51	1.30	0.64	0.70	

Table 3. Value comparison of  $t_{90}$  and dynamic parameters of the following models: Rechnitz-Hameka (ReHa), Lindner (Lind), Shatkay (Shat), model (10) (with  $k$ ) and model (13) (without  $k$ ) for the sodium ISE. The  $s$  is the quality coefficient.

MODEL	ReHa	Lind	Shat	with $k$	without $k$	$t_{90}$
PARAMETER	<b>One decade increase in activity</b>					
T [s]	0.34	0.59	0.10	0.24; 1.53	0.17; 1.16	1.26
$k$ [1]				7.48		
$s$ [mV]	0.59	0.36	0.62	0.26	0.20	
PARAMETER	<b>One decade decrease in activity</b>					
T [s]	0.53	0.32	0.18	0.27; 1.48	0.11; 0.52	1.35
$k$ [1]				5.03		
$s$ [mV]	0.76	1.11	0.64	0.31	0.75	

## 6. SUMMARY

Semi-empirical simplification of the dynamic model (7) leads to two dynamic models: 1) containing the  $k$  parameter and 2) arising from interconnection of two well-known dynamic models. Simulations and experimental research proved that these new models better fit the real dynamic responses of ISE than the well-known ones. The dynamic parameters of a model with the parameter  $k$  are least dependent on the value and direction of activity change in the sample. Therefore, this model should be used to predict the steady-state value of the response in measurements. The value of dynamic parameters of other models as well as the practical response time  $t_{90}$  are much more variable and therefore they characterize ion-selective electrodes worse.

Both the model (7) as well as the two simplified models take into consideration not only the physicochemical phenomena taking place near the electrode's membrane but also the interface electronics of the ion-meter. Such an approach is not yet known in literature.

A serious problem during the research on dynamics of ISE is proper generation of an ion activity step. Mixing of two different samples flowing through the valve and measuring duct causes deformation of the step. The next problem is connected with an application of ion-meters which are characterised by a very high input impedance (e.g.  $10^{12} \Omega$ ). Even a small capacity can then significantly increase the response time of the ISEs.

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