MASARYKOVA UNIVERZITA

Přírodovědecká fakulta

Letní elektrochemická škola

Summer electrochemical school

Zpracováno za přispění **CEITEC**, CZ. 1.05/1.1.00/02.0068,
projektů: **MUNI**/A/0972/2013 a LH 13053 **KONTAKT II** od
MŠMT ČR, **POSTDOC I**, No. CZ.1.07/2.3.00/30.0009

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Úlohy pro letní elektrochemickou školu

Summer electrochemical school tasks

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POTENTIOMETRIC TITRATION

Determination of protonation constants of adenine

Potentiometry is one of the most simple electroanalytical techniques, being primarily used for pH measurements in different samples and for the determination of ionic constituents in biological fluids (e. g. blood, urine), but also as a transduction mode in monitoring selective interactions in molecular sensor devices or in the course of chemical reactions. One of the major types of potentiometry, potentiometric titration is based on the monitoring of the working electrode potential change as a function of the reagent addition to the sample. Potentiometric methods are used for different types of titration (e.g. acidobasic titrations, complexing, redox, precipitation). The result is the potentiometric titration curve of the characteristic sigmoidal shape and the titration endpoint is determined by using different mathematical methods, such as second derivative of titration points, linearization of titration curve (Gran's method), calculation of polynom (Samsonk's method)[1,2].

Potentiometric titration is suitable method for the investigation of protonation – deprotonation equilibrium of biologicaly important compounds (purine derivatives, cytokinins, etc.) and it enables very precisely determination of protonation constants p$K_{a.}$

Adenine (6-aminopurine) is one of the two most commonly occurring purines in a ribonucleic acid (RNA) and deoxyribonucleic acid (DNA), and thus is involved in the process of protein synthesis and transmission of genetic information. The knowledge of its protonation equilibrium is very important not only in biochemical processes and in electroanalysis, but also for the study of metal complexes in which adenine takes the role of the ligand. Adenine exhibits two dissociation constants (pK_{a1} = 4.12 and pK_{a2} = 9.83) [3]

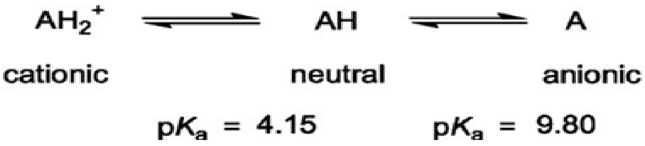

Fig.1: Protonation-deprotonation of adenine

APPARATUS, ACCESSORIES AND REAGENTS

- automatic titrator Titrando 835 (Metrohm, Switzerland), thermostat Julabo F25 – EH
- Tiamo 01/02 software (Metrohm, Switzerland)
- combined ion – selective electrode LL Ecotrode plus

- potentiometric vessel
- argon
- factorized NaOH; HCl; NaCl; milli Q water (18.2 MΩ·cm, 25 °C)
- adenine

SOLUTIONS

Stock solutions

c (NaOH) = 0.1 mol/L; c (HCl) = 0.1 mol/L; c (NaCl) = 1 mol/L; c (adenine) = $1 \cdot 10^{-3}$ mol/L

The LL Ecotrode plus electrode calibration

5 mL of HCl + 4.5 mL of NaCl + 40.5 mL of milli Q water

Sample measurement

0.5 mL of HCl (0,1mol/L) + 5 mL of adenine (mmol/L) + 4.95 mL of NaCl (1 mol/L) + 39.55 mL of milli Q water

EXPERIMENT

The LL Ecotrode plus *electrode calibration*

5 mL of HCl (0.1mol/L); 4.5 mL of NaCl (1mol/L) + 40.5 mL of milli Q water

Sample measurement

0.5 mL of HCl (0.1mol/L) + 5 mL of adenine (mmol/L) + 4.95 mL of NaCl (1 mol/L) +39.55 mL of milli Q water

PARAMETERS

1) *Electrode calibration*: the addition of standard titrant solution (0.1M NaOH) = 0.01 mL ; the total volume of 0.1M NaOH = 10 mL; the dosing rate is “maximal” and the titration mode is set as “optimal”. Other parameters are “0” or “off”

2) *Sample measurement:* the addition of 0.1M NaOH = 0.001 mL; the total volume of 0.1M NaOH = 1 mL; the dosing rate is “maximal” and the titration mode is set as “optimal”. Other parameters are “0” or “off”

Inert atmosphere ensured by bubbling with argon (99.999%) and stirring (magnetic stirrer, speed 3); temperature 25 °C.

MEASUREMENT

a) Start PC, open Tiamo 1.2 software (see manual below) and clean the automatic burette system with standard titrant solution (10 mL of 0.1 mol/L NaOH).

b) Prepare measured solution (for electrode calibration or sample measurement) in the vessel, put LL Ecotrode and dosing capillary into the vessel. Ensure inert atmosphere (bubbling and stirring). c) Set titration parameters in the selected method.

d) Start the measurement.

e) Record the titration curve and export data.

Note: LL Electrode plus is filled by 3M KCl, the filing hole should be opened during the measurement. After measurement don´t let the electrode for long time in basic solution, clean it and put it in stock solution (3M KCl).

POTENTIOMETRIC CURVE EVALUATION

The acidic part of calibration curve is used for determination the slope (q) and equilibrium potential (E^0) by linear regression. The equivalence point allows to calculate concentration of HCl. The basic part of calibration curve help to calculate pK_w (should be for temperature 25° C about 13.78). All these values are important for calculation of pH and degree of titration z and subsequently of pKa value based on these equations:

$$pKa_1 = -\log\left[H^+\right] - \log\left(\frac{z}{1-z}\right) - \log\frac{\gamma_A}{\gamma_{HA}} \qquad pKa_2 = -\log\left[H^+\right] - \log\left(\frac{1-z}{z}\right) - \log\frac{\gamma_{A^-}}{\gamma_A}$$

$$z = \frac{\left(\frac{c_{NaOH}\cdot V_{ekv} - c_{NaOH}\cdot \Delta V}{V_{celk}+\Delta V} - \left[H^+\right] + \left[OH^-\right]\right)}{\left(\frac{c_L}{V_{celk}+\Delta V}\right)}$$

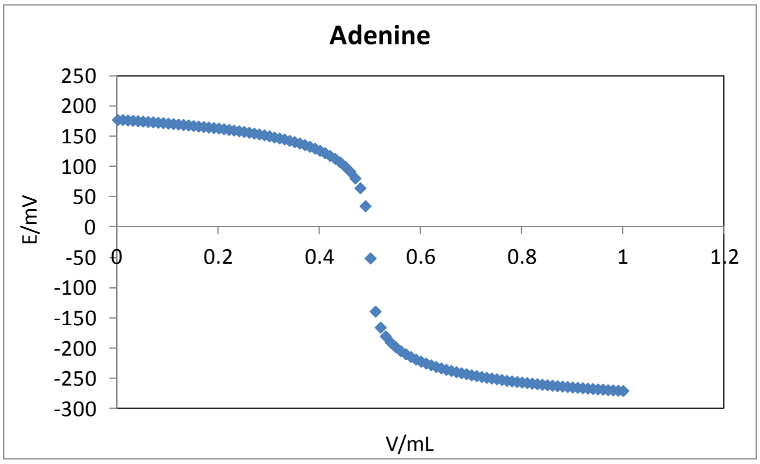

Fig.1: An example of measured data - titration curve of adenine in water

RESULTS AND REPORT

Calibration	
slope q	**E_0**

Measuring		
	pK_{a1}	**pK_{a2}**
1.		
2.		
3.		

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DISCUSSION AND REMARKS

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DISCUSSION AND REMARKS

VOLTAMMETRY ON SOLID STATE ELECTRODES

Electrochemical detection of purine derivatives on the pencil graphite electrode

Linear sweep voltammetry (LSV) is one of most used electrochemical methods. It requires a good potentiostat and three electrode set, which consists of a working electrode, an auxiliary electrode, and a reference electrode. The current is measured between the working and an auxiliary electrode while the potential between the working electrode and a reference electrode is swept linearly in time. The slope of the potential vs. time is called the scan rate *v* and the polarization process can be described by the equation: $E = E_{initial} + vt$. The oxidation or reduction processes of electro-active species are registered as current maxima (peaks I_p) providing the determination of their concentration in solutions.

$$I_p=2.99\cdot 10^5 n(\alpha n_a)^{1/2} A D^{1/2} c v^{1/2} \quad \text{(Delahay equation)}$$

Where: I_p stands for the current peak, n stands for the number of electrons participating in reaction and n_a for the number of electrons participating in a rate determining step, α is the electron transfer coefficient, A is the effective area of electrode, D is the diffusion coefficient, c is the concentration, v is the scan rate.

Purines provide on the pencil graphite electrode (PeGE) in voltammetry well readable oxidation signals. Our research showed that the oxidation response of purines can be increased by using an electro-catalytical effect of monovalent copper ions. Cu(I)ions, obtained by the reduction of Cu(II) *in situ* on PeGE surface, are capable to form a Cu(I)-purine complex and this complex increases surface concentration of the purine studied. Thus, the electroanalysis of adenine, guanine or xanthine with the use of monovalent copper are based on: 1) the electrochemical reduction of Cu(II) at potential -0.1 V, 2) the formation of Cu(I)-purine complex, 3) the oxidation of complex at potentials closed to 0.5 V, 4) the oxidation of purine whose signal is higher than one without the presence of copper ions. The application of copper ions in voltammetric experiments contributes to significant decrease of the detection limit of purine [1-3].

APPARATUS, ACCESSORIES AND REAGENTS

- AUTOLAB PGS30 Analyzer (EcoChemie, Netherlands)
- NOVA software (Metrohm, Switzerland)
- Electrodes (working - PeGE with leads Tombow, 0.5 mm, reference – Ag/Ag Cl/3M KCl, counter electrode – Pt); voltammetric vessel
- argon
- phosphate-acetate buffer pH 5.5; c (CH_3COOH) = 0.4 mol/L, c (H_3PO_4) = 0.4 mol/L, c(NaOH) = 2 mol/L
- adenine, guanine or other purine derivative, copper sulphate; miliQ water (18.2 MΩ·cm)

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SOLUTIONS

Supporting electrolyte

phosphate-acetate buffer pH 5.5; c (CH_3COOH) = 0.4 mol/L, c (H_3PO_4) = 0.4 mol/L, c(NaOH) = 2 mol/L; $CuSO_4 = 1\cdot10^{-3}$ mol/L

Samples

adenine, guanine or xanthine (stock solution = $1\cdot10^{-3}$ mol/L)

EXPERIMENT

- Voltammetric experiment of purine derivate in the absence of copper ions
  2 mL supporting electrolyte + 8 mL miliQ H_2O + 100 µL purine
- Voltammetric experiment of purine derivative in the presence of copper ions
- 2 mL supporting electrolyte + 8 mL miliQ H_2O + 100 µL of purine + 100 µL Cu(II)

PARAMETERS (CV OR LSV - CYCLIC OR LINEAR SWEEP VOLTAMMETRY)

LSV measurement

Start potential -0.1 V; stop potential -0.2 V; upper vertex potential 1.4 V; lower vertex potential -0.1 V; scan rate 200 (400, 800) mV/s; time of accumulation 120 s, room temperature

MEASUREMENT

a) Clean voltammetric vessel (diluted nitric acid, than miliQ water); add 2 mL of supporting electrolyte, 8 mL miliQ H_2O and 100 µL of Adenine or Guanine.
b) Insert working electrode into pencil and connect all electrodes.
c) Perform three electrode set into the measuring vessel with solution of sample.
d) Record the voltammogram with the specified voltammetric parameters.
e) Smooth voltammetric curves by Savitzky-Golay filter (level 2).
f) Save the smoothed curves.
g) Add 100 µL of Cu(II) solution into solution of sample and record LSV curves with the specified parameters.
h) Smooth voltammetric curves by Savitzky-Golay filter (level 2).
i) Save the smoothed curves.
j) Load overlay total voltammograms from all experiments and compare them.

CURVE EVALUATION

Evaluate the peak potential and the peak height of the purine derivative (adenine, guanine or xanthine) in the absence and in the presence of Cu(II) ions.

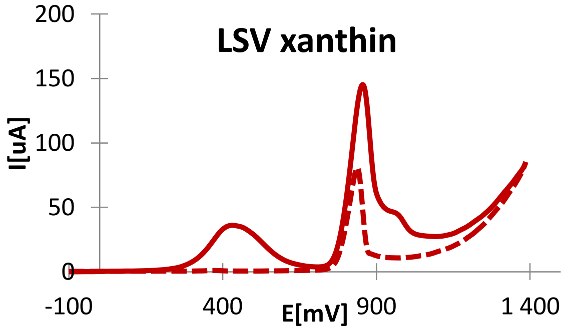

Fig. 1: Real voltammogram of purine (Xan in the absence (dashed line) and in presence (full line) of Cu(II) ions

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a) The evaluation of CV peak height and peak potential for both measurements (with and without Cu(II) ions) for different scan rates (from 50mV/s to 800 mV/s per 50 mV/s).
b) The assessment of the influence of scan rate and Cu(II) ions on peak height and potential.
c) The determination of rate determining step in oxidation of adenine or guanine (see Delahay equation).
d) The evaluation of oxidation process of purine derivative without Cu(I) and with Cu(I)

RESULTS

without Cu		
scan rate (mV/s)	E (V)	I(A)

with Cu		
scan rate (mV/s)	E (V)	I(A)

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DISCUSSION AND REMARKS

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DISCUSSION AND REMARKS

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ELIMINATION VOLTAMMETRIC PROCEDURE (EVP)

The application of different elimination functions to chosen voltammetric curves

The elimination voltammetric procedure (EVP) is a mathematical processing of voltammetric data enabling achievement of better sensitivity and detection limits of studied compounds compared to voltammetric methods on which it relies. It works with elimination voltammetric functions (EVF), eliminating or conserving some chosen partial currents. EVP is based on different dependences of these partial currents on scan rate. In other words, the variable parameter is the scan rate and EVF are presented as linear combinations of total currents measured at different scan rates. In EVP must be satisfied two necessary conditions:

1) An eliminated current can be expressed as a product of two independent functions - the scan rate function and electrode potential function.

$$I_j = Y_j(E) \cdot W_j(\nu)$$

where $Y_j(E)$ is potential function and $W_j(\nu)$ is scan rate function.

2) A total voltammetric current is expressed as a sum of partial currents.

$$I = \sum_{j=1}^{n} I_j = I_d + I_c + I_k + \ldots$$

where I_d is the diffusion current, I_c the charging current and I_k the kinetic current.

Advantages of the approach consist in simplicity and availability. EVP is not time consuming procedure and it is able: (i) to provide better sensitivity, (ii) uncover of minor processes hidden in major processes, (iii) to extend potential range and (iv) to yield new information about electrode processes. The interaction of partial currents can be considered as a partial drawback. This disadvantage is sometimes reflected in an elimination signal distortion, as for example in the case of strongly adsorbed electroactive substances. Then the disadvantage is changed in the advantage because the elimination signal is much more higher and has the form (peak-counterpeak) which does not need a baseline correction [1].

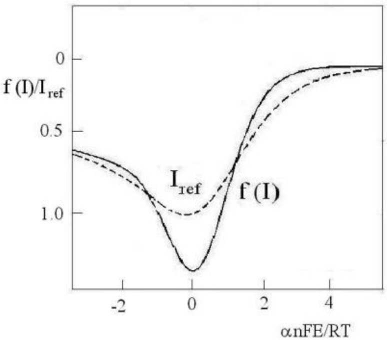

Fig.1: A substance transported to an electrode only by diffusion

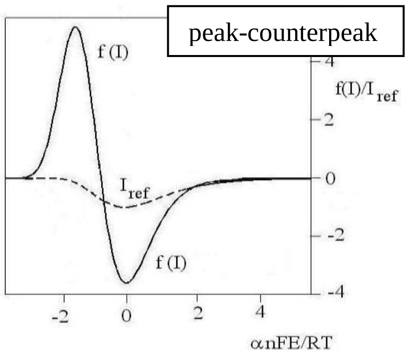

Fig.2: A totally adsorbed electroactive substances

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I_{ref} – reference current, $f(I)$ – the aplication of the elimination function E4 ($I_k + I_c$ elimination and I_d conservation), the values on the axe x are dimensionless.

elimination function E4: $f(I) = a_1 I_{(v1/2)} + a_2 I_{(v)} + a_3 I_{(v2)}$

$$f(I) = -11.657I_{1/2} + 17.485I - 5.8284I_2$$

- Export data from NOVA 1.10 (or GPES) to Excel.
- Use elimination voltammetric procedure EPV E4 for measured data

PARAMETERS

- Scan rates with integer 2: e.g., 100, 200, 400 and 800 mV/s
- Elimination voltammetric functions with calculated coefficients

f(I)	Characteristics	EVLS equation
E1	**$I_d \neq 0$; $I_k = 0$ (I_c dist. By 1.707)**	**$f(I) = -3.4142 \cdot I_{1/2} + 3.4142 \cdot I$**
E2	**$I_d \neq 0$; $I_c = 0$ (I_k dist. By 2.414)**	**$f(I) = 4.8284 \cdot I_{1/2} - 2.4142 \cdot I$**
E3	**$I_k \neq 0$; $I_d = 0$ (I_c dist. By -0.707)**	**$f(I) = 3.4142 \cdot I_{1/2} - 2.4142 \cdot I$**
E4	**$I_d \neq 0$; $I_k = 0$; $I_c = 0$**	**$f(I) = -11.657 \cdot I_{1/2} + 17.485 \cdot I - 5.8284 \cdot I_2$**
E5	**$I_k \neq 0$; $I_d = 0$; $I_c = 0$**	**$f(I) = 6.8284 \cdot I_{1/2} - 8.2426 \cdot I + 2.4142 \cdot I_2$**
E6	**$I_c \neq 0$; $I_d = 0$; $I_k = 0$**	**$f(I) = 4.8284 \cdot I_{1/2} - 8.2426 \cdot I + 3.4142 \cdot I_2$**

CURVE EVALUATION

- Evaluate the EVP curves of the adenine in the absence and in the presence of Cu(II) ions

$$\boxed{\beta_{EVP} = \frac{f(I)}{I}}$$

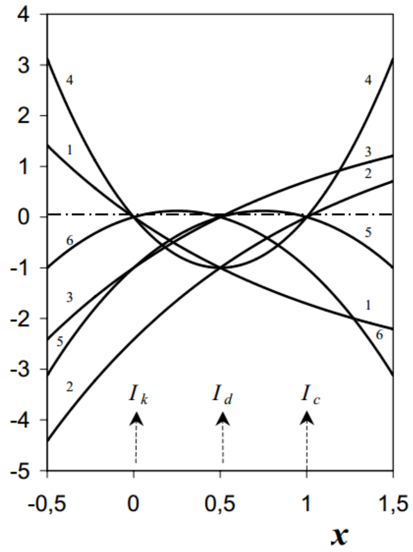

Fig. 3: Dependence of elimination current coefficient β_{EVP} on scan rate coefficient x for EVFs

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RESULTS

without Cu	
method	**I(A)**
CV (LSV)	
EVP	

with Cu	
method	**I(A)**
CV (LSV)	
EVP	

REFERENCES

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DISCUSSION AND REMARKS

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DISCUSSION AND REMARKS

CORROSION

Determination of corrosion rate of steel samples in different environments by linear polarization assessed by Tafel equation

The simplest definition of corrosion is: It is the process of a metal returning to the material's thermodynamic state. Most of the materials form the oxides or sulfides from which they were originally in the earth. In the other words, corrosion is the gradual destruction of materials (usually metals) by reduction-oxidation reactions:

Anode: $M^o - ne \rightarrow M^{n+}$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (in alkaline solutions)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (in acidic solutions)
$2H^+ + 2e \rightarrow H_2$

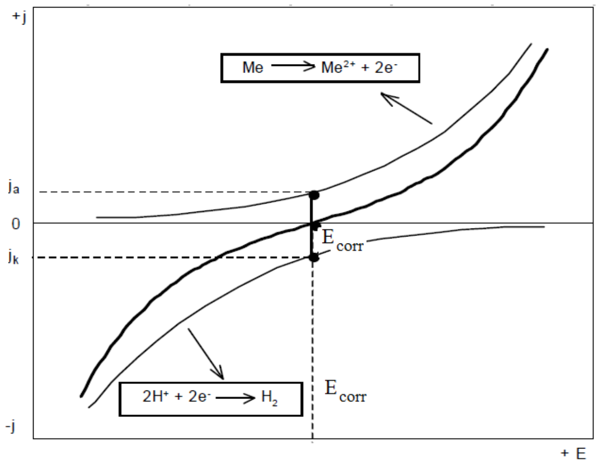

Fig. 1: The combination of anodic polarization curve with current density j_a (metal ionization) and cathodic polarization curve with current density j_c (cation reduction and hydrogen depolarization). The bold line represents the sum of both processes.

Most corrosion phenomena are of electrochemical nature and consists of two (or more) electrode reactions on the surface of corroding material. One possible reaction is the oxidation of metal (e.g., metal or steel dissolution) refers to anodic partial reaction and the other one is the reduction reaction (e.g., reduction of oxygen) which refers to cathodic partial reaction. Non-electrochemical reaction between products of these reactions forms the final product (e.g., rust). To determine the corrosion rate, depending on kinetics of both cathodic and anodic reactions, we obey Faraday's law, where the linear relationship exists between the metal dissolution rate at some potential and the partial anodic current density for metal dissolution. If there is no external polarization, the metal spontaneously gains a certain potential (corrosion potential – E_{corr}) in contact with an oxidizing electrolytic environment. The partial anodic current density at the E_{corr} refers to the corrosion current density i_{corr}.

$$E_{corr}=i_{corr}/nF$$

Where n is the chargé number (number of electrons exchanged in dissolution reaction), F is the Faraday's constant (F = 96.485 C/mol). The E_{corr} can be obtained between the equilibrium potentials of the anodic and cathodic partial reactions, which could be predicted by electrochemical thermodynamics [1-3].

To slow down the corrosion rate we use several types of inhibitors. We distinguish these types of inhibitors: anodic, cathodic, mixed and volatile corrosion inhibitors (VCI). Anodic inhibitors usually form the protective oxide film on the metal surface. Cathodic inhibitors

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slower the cathodic reaction or selectively precipitate on the surface area to decrease the diffusion of reducing substances to the surface. Mixed inhibitors reduce both cathodic and anodic reactions via film forming compounds. VCI (also called Vapor Phase Inhibitors) are compounds transported in a closed environment to the site of corrosion by vaporizing from the source [4].

Steel materials are subject to corrosion and loose some attributes caused by their oxidation depending on time. Studied material is subjected to linear polarization (LSV - Linear Sweep Voltammetry) and LSV curves are processed using the Tafel slope analysis providing not only a corrosion rate, but also a corrosion potential, a current density and a polarization resistance. These results enable to compare different corrosive materials and effects of corrosion accelerators or inhibitors in different environment.

Linear polarization evaluation and Tafel slope analysis are described on http://www.ecochemie.nl/Applications/.

CALCULATION OF CORROSION RATES

The corrosion rate depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions. According to Faraday's law, there is a linear relationship between the metal dissolution rate or corrosion rate, R_M, and the corrosion current density i_{corr}:

$$R_M = \frac{M}{nF\rho} i_{corr}$$

The relationship between current density and potential of anodic and cathodic electrode reactions under charge transfer control is given by the Butler-Volmer equation:

$$i = i_{corr} (e^{2.303\frac{\eta}{b_a}} - e^{2.303\frac{\eta}{b_c}}) \text{ , where } \eta = E - E_{corr}$$

In the above equation E is the applied potential and i_{corr} the measured current density. The overpotential, η, is defined as the difference between applied potential and the corrosion potential E_{corr}. The corrosion potential, is the open circuit potential (OCP) of a corroding metal. The corrosion current, i_{corr}, and the Tafel constants b_a, and b_c can be measured from the experimental data.

APPARATUS, ACCESSORIES AND REAGENTS

- AUTOLAB PGSTAT101 (Metrohm Switzerland); Corrosion cell 400 ml (Metrohm, Switzerland), Thermostat F12 Julabo (Julabo, Germany)
- Software NOVA 1.10.2 (Metrohm, Switzerland)
- Electrodes (WE – sample (steel); RE – Ag/AgCl/3 M KCl; AE – Stainless steel or Pt)
- NaCl solution, $c_1(NaCl) = 0.15$ mol/L, $c_2(NaCl) = 0.6$ mol/L; mild steel sample (M_r = 55,585)
- Corrosion inhibitor: Adenine or caffeine ($1*10^{-3}$ mol/L)

SOLUTIONS

Supporting electrolyte
0.15 M NaCl solution pH 5,75
0.6 M NaCl solution pH 5,88
Inhibitor solution :1m M adenine or caffeine

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EXPERIMENT

Measuring method: Linear sweep voltammetry (LSV), procedure in NOVA: linear polarization (with open circuit potential - OCP determination)

PARAMETERS

Measuring method: Linear sweep voltammetry (LSV)

Start potential -0.3 V, stop potential 0.3 V, scan rate 5 or 10 m V/s, temperature 25 °C

Make sure that there is no bubble at the end of the salt bridge after supporting electrolyte is poured inside the corrosion cell!

MEASUREMENT

a) There are sample of mild steel circuits available. Clean them by scratching the measuring side with sandpaper 21111 2/0 than wash it in acetone.
b) Insert mild steel circuit into measuring cell and connect as working electrode
c) Pour the supporting electrolyte (400 mL) into the corrosion cell and plug reference electrode and auxiliary electrode
d) Set the temperature on the thermostat to 25 °C and wait until the temperature inside the corrosion cell is stabilized.
e) Record the linear polarization voltammogram with the specified parameters. Save the voltammogram together with method parameters
f) Repeat step a) to e) with all samples.

CURVE EVALUATION

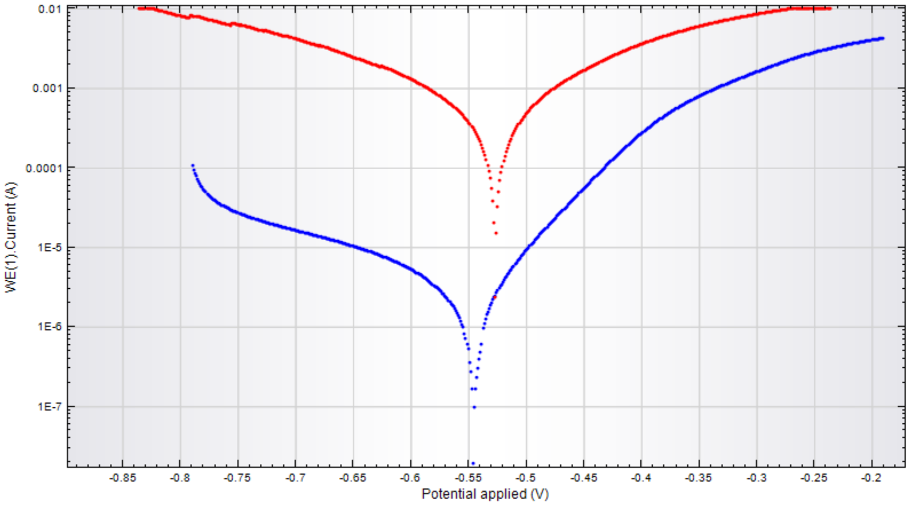

Fig. 2: Real voltammograms comparison of mild steel samples in different environments: Saline solution (blue), 0.1 M H_2SO_4 (red).

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RESULTS

Solution	Ecor [V]	icor [A]	jcor [A/cm2]	Polarizationresistence [Ω]	Corrosion rate [mm/year]
0.9 % NaCl					
3.5 % NaCl					
0.9 % NaCl + inhibitor					
3.5 % NaCl + inhibitor					
0.9 % NaCl + inhibitor					
3.5 % NaCl + inhibitor					

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DISCUSSION AND REMARKS

Zpracováno za přispění **CEITEC**, CZ. 1.05/1.1.00/02.0068, projektů: **MUNI**/A/0972/2013 a LH 13053 **KONTAKT II** od MŠMT ČR, **POSTDOC I**, No. CZ.1.07/2.3.00/30.0009

DISCUSSION AND REMARKS

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

EIS of guanine on modified and unmodified graphite electrodes

Electrochemical Impedance Spectroscopy (EIS) is a powerful technique for the characterization of electrochemical systems. The promise of EIS is that, with a single experimental procedure encompassing a sufficiently broad range of frequencies, the influence of the governing physical and chemical phenomena may be isolated and distinguished at a given applied potential.

In recent years, EIS has found widespread applications in the field of characterization of materials. It is routinely used in the characterization of coatings, batteries, fuel cells, and corrosion phenomena. It has also been used extensively as a tool for investigating mechanisms in electro–deposition, electro–dissolution, passivity, and corrosion studies. It is gaining popularity in the investigation of diffusion of ions across membranes and in the study of semiconductor interfaces.

Principles of EIS measurements

The fundamental approach of all impedance methods is to apply a small amplitude sinusoidal excitation signal to the system under investigation and measure the response (current or voltage or another signal of interest1). In the following figure, a non-linear i-E curve for a theoretical electrochemical system is shown in Figure 1.

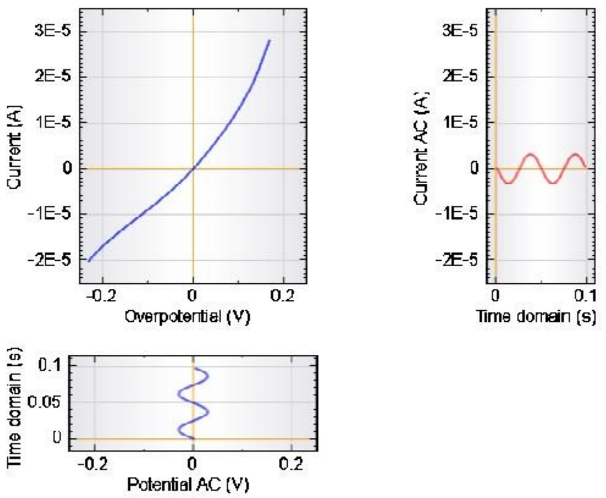


Fig. 1: Potential and current modulation recorded during an impedance measurement

A low amplitude sine-wave $\Delta E\cdot\sin(\omega t)$, of a particular frequency ω, is superimposed on the DC polarization voltage E_O. This results in a current response of a sine wave superimposed on the DC current $\Delta i\cdot\sin(\omega t+\varphi)$. The current response is shifted with respect to the applied potential (see Figure 2).

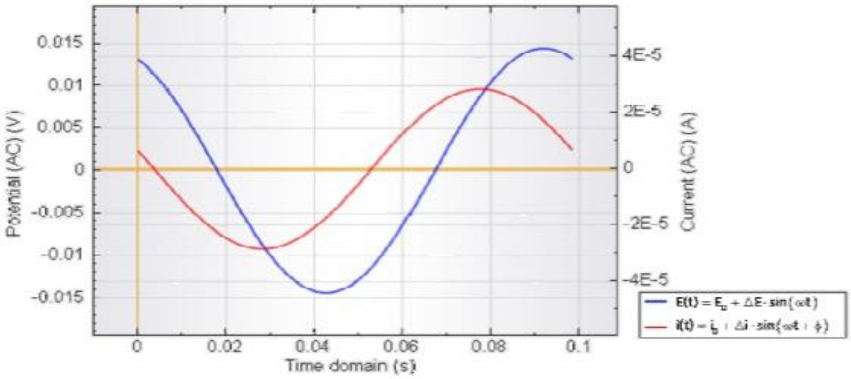


Fig. 2: Time domain plots of the low amplitude AC modulation and response

The Taylor series expansion for the current is given by:

$$\Delta i = \left(\frac{di}{dE}\right)_{E_o, i_o} \Delta E + \left(\frac{d^2 i}{dE^2}\right)_{E_o, i_o} \Delta E^2 + \ldots..$$

If the magnitude of the perturbing signal ΔE is small, then the response can be considered linear in first approximation. The higher order terms in the Taylor series can be assumed to be negligible. The impedance of the system can then be calculated using Ohms law as:

$$Z(\omega) = \frac{E(\omega)}{i(\omega)}$$

This ratio is called impedance, Z(ω), of the system and is a complex quantity with a magnitude and a phase shift which depends on the frequency of the signal. Therefore by varying the frequency of the applied signal one can get the impedance of the system as a function of frequency. Typically in electrochemistry, a frequency range of 100 kHz – 0.1 Hz is used. The impedance Z(ω), as mentioned above is a complex quantity and can be represented in Cartesian as well as polar coordinates. In polar coordinates the impedance of the data is represented by:

$$Z(\omega) = \left|Z(\omega)\right| e^{\varphi\omega}$$

Where |Z(ω)| is the magnitude of the impedance and is the phase shift. In Cartesian coordinates the impedance is given by:

$$Z(\omega) = Z'(\omega) - j\,Z''(\omega)$$

Where Z'(ω) is the real part of the impedance and Z"(ω) is the imaginary part and $\overline{\quad}$.

Data presentation

The plot of the real part of impedance against the imaginary part gives a Nyquist plot, as shown in Figure 3. The advantage of Nyquist representation is that it gives a quick overview of the data and one can make some qualitative interpretations. While plotting data in the Nyquist format the real axis must be equal to the imaginary axis so as not to distort the shape of the curve. The shape of the curve is important in making qualitative interpretations of the data. The disadvantage of the Nyquist representation is that one loses the frequency dimension of the data. One way of overcoming this problem is by labeling the frequencies on the curve.

The absolute value of impedance and the phase shifts are plotted as a function of frequency in two different plots giving a Bode plot in Figure 4. This is the more complete way of presenting the data.

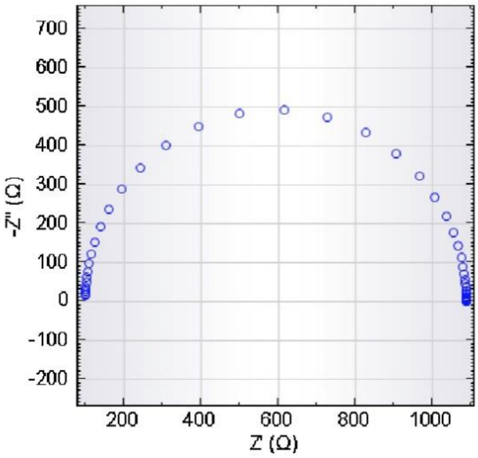


Fig. 3: A typical Nyquist plot

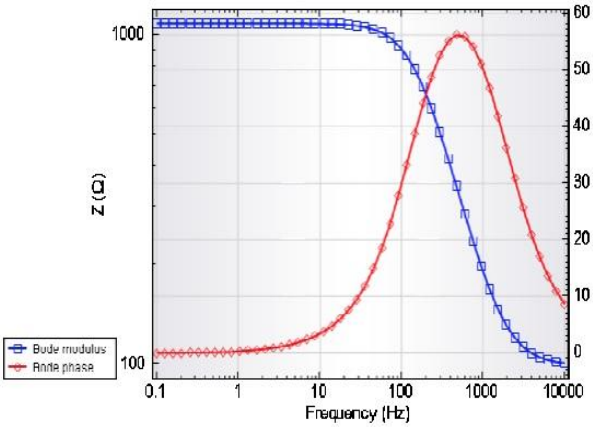


Fig.4: A typical Bode plot

A third data presentation mode involving a 3D plot, is available. In this presentation mode the real and imaginary components are plotted on the X and Y axis, respectively and the logarithm of the frequency is plotted on the Z axis (see Figure 5).

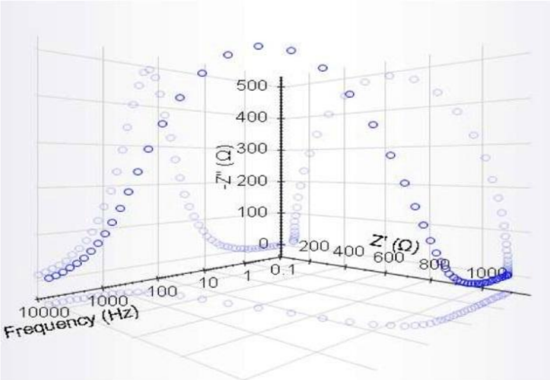


Fig.5: 3D plot

The relationship between the two ways of representing the data is given by:

$$|Z|^2 = (Z')^2 + (-Z'')^2 \qquad tg(\varphi) = \frac{-Z''}{Z'}$$

Alternatively, the real and imaginary components can be obtain from:

$$Z' = |Z|\cos\varphi \quad \text{and} \quad -Z'' = -|Z|\sin\varphi$$

APPARATUS, ACCESSORIES AND REAGENTS

- AUTOLAB PGSTAT20 Analyzer (Metrohm AUTOLAB, Netherlands)
- NOVA software 1.10
- Electrodes (working - PeGE with leads Tombow, 0.5 mm, reference – Ag/Ag Cl/3M KCl, counter electrode – Pt); voltammetric vessel
- argon
- phosphate-acetate buffer pH 5.5; c (CH_3COOH) =0.4 mol/L, c (H_3PO_4)=0.4 mol/L, c(NaOH)=2 mol/L
- adenine; copper sulphate; miliQ water (18.2 MΩ·cm)

SOLUTIONS

Supporting electrolyte

phosphate-acetate buffer pH 5.5; c (CH_3COOH) =0.4 mol/L, c (H_3PO_4)=0.4 mol/L, c(NaOH)=2 mol/L, c($CuSO_4$)=$1\cdot10^{-3}$ mol/L

Samples

adenine = $1\cdot10^{-3}$ mol/L; (or guanine)

EXPERIMENT

- EIS experiment for adenine in the absence of copper ions – 2 mL supporting electrolyte + 8 mL miliQ H_2O + 100 µL adenine (guanine)

PARAMETERS

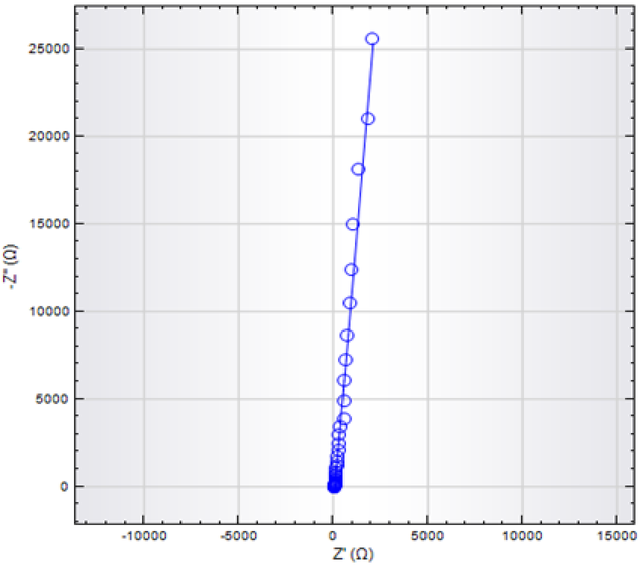
- Measuring method potentiometric electrochemical impedance spectroscopy
- Start 0.1 V, End potential 1.2V, logarithmic step 0.2V
- Frequency 10 000- 0.1 Hz, 50 steps (logarithmic)
- RPM 0.1V

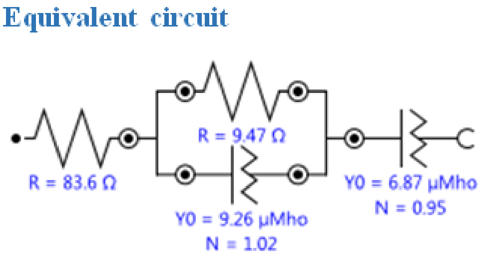
MEASUREMENT

a) Clean voltammetric vessel (diluted nitric acid, than miliQ water). Than we added in the vessel 2 mL of supporting electrolyte, 8 mL miliQ H_2O and 100 µL of adenine (guanine)
b) Insert working electrode into pencil and connect all electrodes.
c) Start potentiometric EIS
d) Save data
e) Data analysis, Fit and Simulation
f) Insert equivalent circuit and Fit data
g) Export results

Measured data

Equivalent circuit





Results

Element	Parameter	Value
R1	R	83.613
R2	R	9.4724
Q1	Y0	9.2585E-06
	N	1.0198
Q2	Y0	6.8726E-06
	N	0.94971
	χ^2	0.033201

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DISCUSSION AND REMARKS

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Letní elektrochemická škola

Summer electrochemical school

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