



Pseudopolarography of trace metals. Part II. The comparison of the reversible, quasireversible and irreversible electrode reactions

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Abstract

The theoretical and experimental pseudopolarographic curves of reversible, quasireversible and irreversible electrochemical reactions were compared and evaluated. The measurements were performed on a stationary mercury drop electrode (SMDE, PAR 303A), using differential pulse anodic stripping voltammetry (DPASV). A good agreement between the theoretical and the experimental shift of the half-wave potential with an increasing accumulation time was obtained for the reversible pseudopolarograms of 10^{-7} mol dm⁻³ Cd(II) (in 0.1 mol dm⁻³ NaClO₄, pH ~2). As compared with the curve of the logarithmic analysis of the polarogram, the corresponding curve of the pseudopolarogram is steeper in the region of the half-wave potential. It has been shown that even though the pseudopolarograms are quasireversible or irreversible, there is a range at the foot of the curves with a reversible slope (usually below 10% of the total/limiting current). It has been verified that the range of this reversible slope can be extended by increasing the accumulation time, lowering the mercury drop size and diminishing the thickness of the diffusion layer. The estimated value for its approximative evaluation is about 1% of the total/limiting current. This is essential for the determination of the corresponding electrochemical parameters, such as: the formal potential ($E^{o'}$), transfer coefficient (α) and rate constant (k_s). From the experimentally obtained reversible slope of the (pseudo)polarographic curves of Zn(II) (in 1 mol dm⁻³ NaClO₄, pH 4.7 ± 0.1), the parameters for the quasireversible electrochemical reactions were estimated as follows: $E^{o'} = -0.964 \pm 0.002$ V, $\alpha = 0.24 \pm 0.02$ and $k_s \sim 2-3 \times 10^{-3}$ cm s⁻¹. It is shown that an accurate transfer coefficient can be calculated from the curves of the logarithmic analysis of the quasireversible pseudopolarograms, which is not the case for the polarographic curves. The irreversible system, tested on the electrochemical reaction of the CdNTA complex (in 0.1 mol dm⁻³ NaClO₄, pH 7.9 ± 0.1), shows relatively good agreement between the experimental and the theoretical dependences. The (pseudo)polarographic measurements enabled approximate estimation of the electrochemical parameters ($E^{o'} = -0.835 \pm 0.010$ V, $\alpha = 0.55 \pm 0.02$ and $k_s = 1.0 \pm 0.4 \times 10^{-4}$ cm s⁻¹) which are in fairly good agreement with the literature data.

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1. Introduction

Pseudopolarography is the only direct analytical method which allows the measurement of dissolved trace metal speciation at natural concentration levels. The method was introduced more than 30 years ago [1–7], and is based on anodic stripping voltammetry (ASV). The sigmoidally shaped curve, constructed from the ASV peak currents at various accumulation potentials, is called a pseudopolarogram. The theory of pseudo-

polarography for reversible [3,4,6–8] and non-reversible [4,6–8] electrode reactions utilizing a mercury drop electrode (MDE) [3,4,8], a thin mercury film electrode TMFE [6,7,9], and an ultra microelectrode UME [10] has been proposed. The latest theories of pseudopolarography for a thin mercury film electrode (TMF), and for stripping chronopotentiometry at a scanned deposition potential (SSCP), were proposed by Lovrić [11] and by van Leeuwen and Town [12], respectively. Pseudopolarography is used for the complexation studies of both labile [1,2,5–7,12–21] and inert metal species [8,20–24]. It was shown that a pseudopolarographic approach can be applied to speciation studies of

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reversible [1,2,5–9,13,14,21], quasireversible [15–17] and irreversible electrochemical reactions [6,21–25]. The methods developed for trace metal speciation using classic polarographic data (at high metal concentration; e.g., the DeFord–Hume method [26]), are also relevant to pseudopolarography. Two main principles were used as a basis for the speciation studies using pseudopolarographic data. The first principle is based on the shift of the half-wave potential of the pseudopolarogram with the addition of the complexing ligand forming labile [1,2,5–7,12–21] or inert complexes [22–24]. The second is based on the ratio of the two signals: the free/labile complex and the inert metal complex [27,28]. The application of pseudopolarography for trace metal speciation using a TMFE and a HMDE, as well as various aspects of the experimental pseudopolarography (both the measurements and the data processing) are described fully in the papers by Komorsky-Lovrić et al. [15] and Town and Fillela [21], respectively.

Numerous papers describe the methods for the determination of the parameters of the electrochemical reaction (reversible/formal potential, transfer coefficient, rate constant), yet only a few papers employ such a characterization using the pseudopolarographic curves [4,7,15,16,18,22]. Even though the theory of pseudopolarography for both the reversible and the non-reversible electrochemical processes is well known, a comprehensive experimental validation of the quasireversible and irreversible systems has not up to now been elaborated and well documented.

In this paper, the main characteristics of the theoretical and the experimental pseudopolarographic curves of reversible, quasireversible and irreversible electrochemical reactions are elaborated and compared in detail. The comparative advantages of the pseudopolarographic approach for the determination of the electrode parameters of non-reversible electrochemical reactions are given. Some useful guidelines for the experimental setup for the pseudopolarographic measurements of the speciation of trace metals are suggested. The simulated polarographic and pseudopolarographic curves are obtained using the theories proposed by Ružić [29] and Shuman and Cromer [4], respectively.

2. Experimental

2.1. Reagents

All electrolyte solutions were prepared in distilled, deionised water from a Milipore Milli-Q system (Bedford, USA) using the chemicals of “analytical-reagent” grade, $\text{Cd}(\text{NO}_3)_2$, H_3BO_3 , $\text{Zn}(\text{NO}_3)_2$, TlNO_3 , NTA, $\text{NaClO}_4 \times \text{H}_2\text{O}$, NaOH and NaCl (Merck, Darmstadt) and “suprapur” concentrated HClO_4 . A stock borate

buffer solution (0.5 M) was prepared by combining boric acid (H_3BO_3) and sodium hydroxide (NaOH) with pH of 7.9 ± 0.1 . An acetate buffer was used for the measurements in the acidic region of $\text{pH } 4.7 \pm 0.1$. The electrolyte solutions in the electrochemical cell were initially purged with oxygen-free nitrogen for at least 15 min, and a nitrogen blanket was maintained during the measurements.

The blank concentrations of the dissolved trace metal impurities (mainly lead and zinc) in the supporting electrolyte were diminished by a potentiostatic electrolysis (reduction) on a Hg-pool cathode using an EG&G potentiostat model PAR 273, as described in detail elsewhere [18].

2.2. Instrumentation

An Ecochemie $\mu\text{AUTOLAB}$ multimode polarograph (Utrecht, The Netherlands) was used for the pseudopolarographic, voltammetric and polarographic measurements. The automatic pseudopolarographic measurements were carried out using newly developed software called PseudoSOFT [18,27]. The electrochemical cell with a three-electrode system was used in all measurements. The working electrode was a static mercury drop electrode (SMDE) PAR 303A with a modified holder for the electrode components [30]. The reference electrode was an $\text{Ag}|\text{AgCl}|(\text{sat. NaCl})$ electrode, and a platinum wire was used as a counter electrode. The electrolyte solution was stirred at 4000 rpm using a quartz rotating stirrer driven by a “Port Escap DC” electromotor controlled by a home-made power supply. The pH was controlled by an Orion Research pH meter (EA 920) with a glass pH electrode.

Differential pulse anodic stripping voltammetry (DPASV) and sampled dc polarography, as a scanning operating mode, were applied under the selected conditions as follows: a deposition potential (E_{dep}), an initial potential (E_i), a final potential (E_f), a differential pulse amplitude (A), a potential step increment ($E_{\text{st inc}}$), an accumulation time (t_{acc}), a time between pulses (t_{int}), a pulse duration (t_{dur}) and a drop time (t_d).

3. Results and discussion

3.1. The shape of the pseudopolarographic curves

Fig. 1 shows the simulated pseudopolarograms for the two-electron charge transfer for the different rate constants (k_s) representing the reversible (curve 1, $\alpha = 0.5$, $k_s = 1 \text{ cm s}^{-1}$), quasireversible (curve 2, $\alpha = 0.5$, $k_s = 1 \times 10^{-3} \text{ cm s}^{-1}$) and irreversible (curves 3 and 4, $\alpha = 0.5$, $k_s = 1 \times 10^{-4} \text{ cm s}^{-1}$, $k_s = 1 \times 10^{-5} \text{ cm s}^{-1}$) electrochemical reactions. Under these simulated conditions, the half-wave potential of the pseudopolaro-

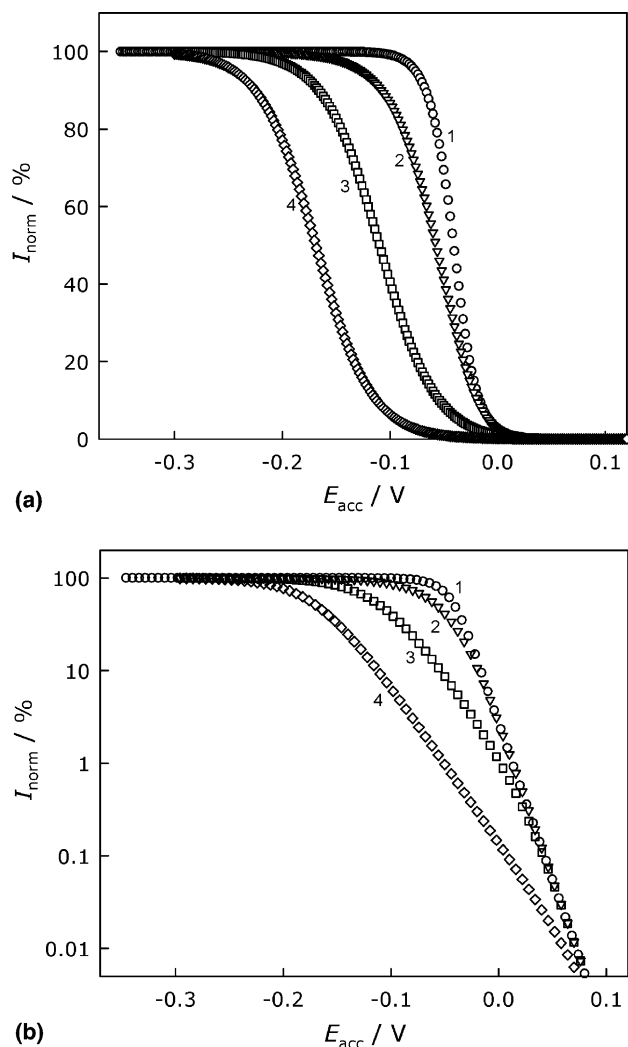


Fig. 1. The simulated reversible ($\alpha = 0.5, k_s = 1 \text{ cm s}^{-1}$; curve 1), quasireversible ($\alpha = 0.5, k_s = 1 \times 10^{-3} \text{ cm s}^{-1}$; curve 2) and irreversible ($\alpha = 0.5, k_s = 1 \times 10^{-4} \text{ cm s}^{-1}$; curve 3 and $\alpha = 0.5, k_s = 1 \times 10^{-5} \text{ cm s}^{-1}$; curve 4) pseudopolarograms for the two-electron charge transfer plotted with linear (a) and logarithmic (b) scales of the normalized current. The simulation parameters: $t_{\text{acc}} = 60 \text{ s}$, $\delta = 1.4 \times 10^{-3} \text{ cm}$, $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $E_{\text{form}} = 0 \text{ V}$, $r_{\text{drop}} = 0.0351 \text{ cm}$.

grams shifts to more negative values with the decrease of the rate constant (k_s), leading to the separation of the reversible and irreversible pseudopolarograms (for about 100 mV). Fig. 1(b) shows the pseudopolarograms plotted on a logarithmic scale of the ordinate within a range of potentials where all three pseudopolarographic curves reach the reversible slope. For the conditions presented, the potentials of the quasireversible and irreversible curves are in the range below 5% and 0.1% of the limiting current, respectively. The corresponding reversible half-wave potential (formal potential) of the experimental curves is determined on the basis of this range. The transfer coefficient and the rate constant can also be estimated by combining the simulated parameters. The main electrochemical parameter for the metal

speciation studies is a reversible half-wave potential ($E_{1/2, \text{rev}}$). The determination of the stability constants of the labile metal complexes using the DeFord–Hume approach [26] involves the electrochemical reversibility of the added ligand in the whole range. Since not all electrochemical reactions show reversible behavior, the potential from the reversible part of the (pseudo)polarographic curve can be utilized as an alternative. The reversible part of the irreversible pseudopolarogram presented is experimentally unobtainable since it is below 0.3% of the limiting current. By lowering the rate constant (curve 4, $k_s = 1 \times 10^{-5} \text{ cm s}^{-1}$), the pseudopolarogram shifts to a more negative potential, without changing the shape. Its reversible part is below 0.01% of the limiting current.

The accumulation time (t_{acc}) is the most variable parameter in the pseudopolarographic measurements. Depending on the reversibility of the electrochemical reaction, the pseudopolarographic half-wave potential ($E_{1/2, \text{pse}}$) shifts to more negative values. Fig. 2 shows the dependence of $E_{1/2, \text{pse}}$ with the increase of the accumulation time for the reversible (1), quasireversible (2) and irreversible (3) electrochemical reactions. This relation is linear for the reversible system for an accumulation time higher than 10 s. Below the accumulation time of 10 s, this relationship is curvilinear approaching a zero value. Fig. 2 also shows that the half-wave potential of the quasireversible electrochemical reaction shifts in a negative direction (about 50 mV) from the reversible half-wave potential and remains unchanged until the accumulation time increases over 10 s. Subsequently, the slope of the curve changes, achieving reversible values at

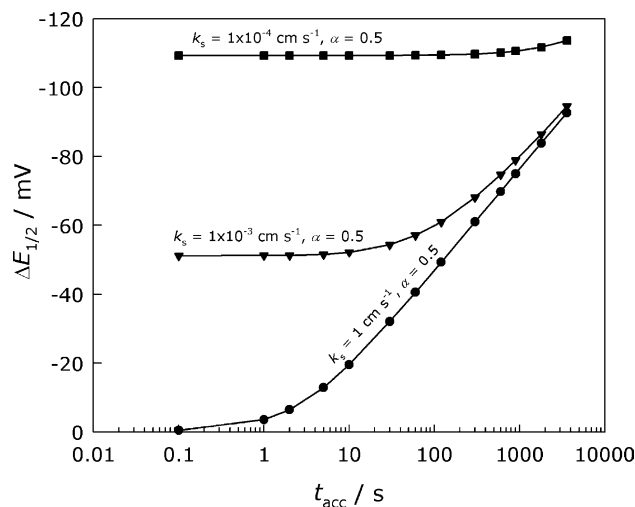


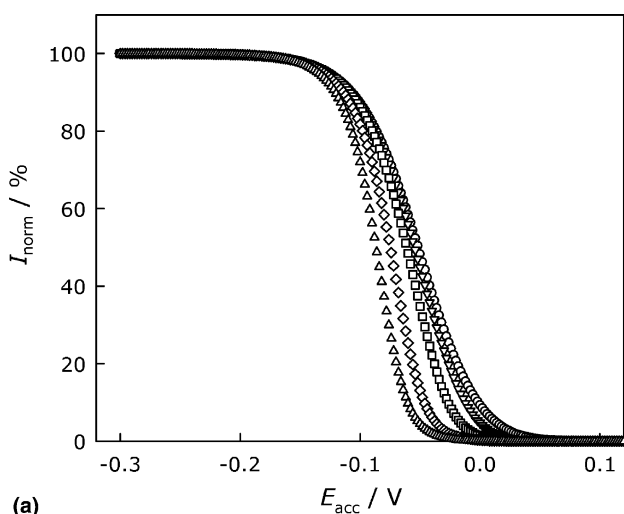
Fig. 2. The dependence of the half-wave potential of the simulated reversible ($\alpha = 0.5, k_s = 1 \text{ cm s}^{-1}$; ●), quasireversible ($\alpha = 0.5, k_s = 1 \times 10^{-3} \text{ cm s}^{-1}$; ▼) and irreversible ($\alpha = 0.5, k_s = 1 \times 10^{-4} \text{ cm s}^{-1}$; ■) pseudopolarograms on the accumulation time (logarithmic scale), for the two-electron charge transfer. The simulation parameters: $\delta = 1.4 \times 10^{-3} \text{ cm}$, $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $E_{\text{form}} = 0 \text{ V}$, $r_{\text{drop}} = 0.0351 \text{ cm}$.

very long accumulation times. The extraction of the reversible part of the quasireversible and irreversible pseudopolarograms (electrochemical reactions) becomes easier and more accurate with a longer accumulation time. The simulated quasireversible pseudopolarograms ($\alpha = 0.5$, $k_s = 1 \times 10^{-3} \text{ cm s}^{-1}$) illustrated in Fig. 3, show that the reversible part extends from about 0.1% at $t_{\text{acc}} = 5 \text{ s}$, to about 15% at $t_{\text{acc}} = 1800 \text{ s}$.

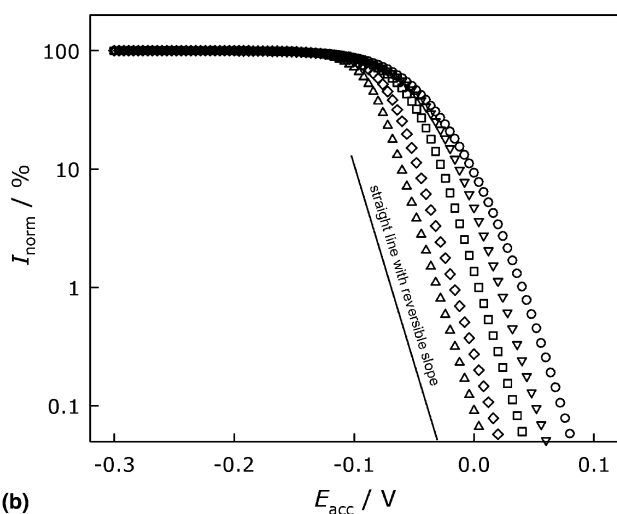
For the irreversible electrochemical reactions ($\alpha = 0.5$, $k_s = 1 \times 10^{-4} \text{ cm s}^{-1}$), the shift of the half-wave potential is observed only for long accumulation times (Fig. 2). At the accumulation time of 900 s, the half-wave potential shifts only 2 mV (as compared to the half-wave potential at the accumulation time of 10 s), which is on the level of an experimental error. However, even though the electrochemical reaction is irreversible,

the parameters of the measurements can be adjusted so as to give pseudopolarograms with the reversible part above 1%. In addition to the accumulation time, the reversible part can be extended using a smaller mercury drop and a thicker diffusion layer (weaker stirring). Fig. 4 shows the irreversible pseudopolarograms ($\alpha = 0.5$, $k_s = 1 \times 10^{-4} \text{ cm s}^{-1}$) simulated with the parameters (mercury radii and diffusion layer thickness) that correspond to a Metrohm mercury drop electrode (VA Stand 663 Multi mode electrode). The pseudopolarograms presented clearly show that the range extends from 0.1% to 2%, which is experimentally attainable.

Assuming the detection limit of the HMDE on the level of the dissolved trace metal concentration of 10^{-11}

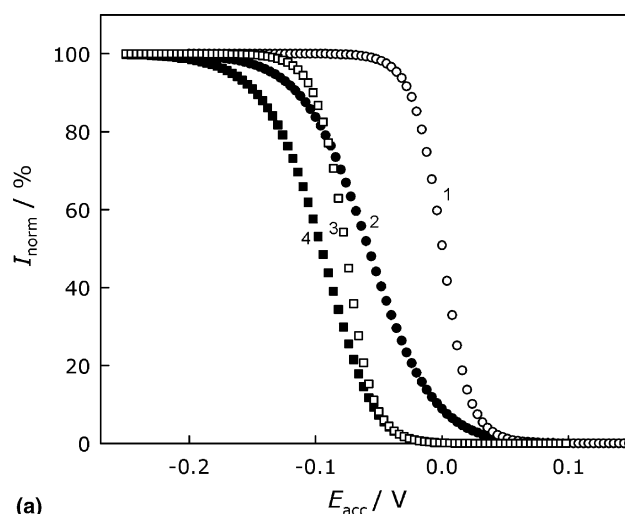


(a)

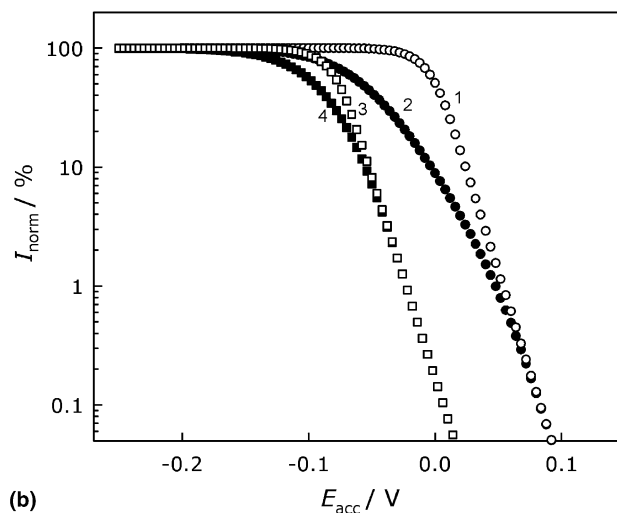


(b)

Fig. 3. Simulated quasireversible pseudopolarograms ($\alpha = 0.5$, $k_s = 1 \times 10^{-3} \text{ cm s}^{-1}$) for two-electron charge transfer with varying accumulation time, (○), 5 s; (∇), 30 s; (□), 120 s; (◇), 600 s; (△), 1800 s, plotted with linear (a) and logarithmic (b) scale of the normalized current. The simulation parameters: $\delta = 1.4 \times 10^{-3} \text{ cm}$, $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $E_{\text{form}} = 0 \text{ V}$, $r_{\text{drop}} = 0.0351 \text{ cm}$.



(a)



(b)

Fig. 4. The simulated irreversible (●, ■; $\alpha = 0.5$, $k_s = 1 \times 10^{-4} \text{ cm s}^{-1}$) and reversible (○, □) pseudopolarograms for two-electron charge transfer plotted with linear (a) and logarithmic (b) scales of the normalized current. The simulation parameters: (○, ●) – $t_{\text{acc}} = 60 \text{ s}$, $\delta = 1.5 \times 10^{-3} \text{ cm}$, $r_{\text{drop}} = 0.016 \text{ cm}$, $E_{\text{form}} = -0.25 \text{ V}$, $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; (□, ■) – $t_{\text{acc}} = 600 \text{ s}$, $\delta = 3.0 \times 10^{-3} \text{ cm}$, $r_{\text{drop}} = 0.010 \text{ cm}$, $E_{\text{form}} = -0.30 \text{ V}$, $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

mol dm⁻³ [31], the lowest concentration of trace metal in the solution that can be measured (presuming precise determination of the peak height of only 1% of total current) is about 10⁻⁹ mol dm⁻³. This concentration is practically in the order of magnitude of trace metal concentrations in natural waters. It is enough low for the representative speciation of trace metals using the proposed pseudopolarographic method. Using an internal standard (redox) process, improved reproducibility can be obtained, which lowers the determination limit, as well. As mentioned above, a longer accumulation time, a smaller drop size and a thicker diffusion layer generate a higher concentration of the metal accumulated in the mercury drop which produces a larger reversible part of the pseudopolarographic curve. Because of the influence of the diffusion layer thickness on the reversibility of the pseudopolarographic curves, better results are obtained by weaker stirring, because the kinetic parameter is less pronounced if a thicker diffusion layer is utilized. These data indicate that microelectrodes are convenient for such pseudopolarographic measurements.

3.2. Reversible electrochemical system

In the first part of this publication sequence [18], some basic aspects of the experimental pseudopolarography of the reversible electrochemical reaction are described. It is shown that the half-wave potential shifts to more negative potentials with increasing accumulation time. As an example, Fig. 5 shows the original (a) and the normalized (b) pseudopolarograms of 10⁻⁷ mol dm⁻³ Cd(II) measured in 0.1 M NaClO₄ (pH 2) with increasing accumulation time. The normalization of the pseudopolarograms is performed as described elsewhere [18]. Using a corrected accumulation time, a linear relationship of the half-wave potential on the increasing accumulation time, with a slope of 0.029 V, was obtained (inset in Fig. 5(b)). Although the reproducibility of the discrete measurement points is relatively poor (especially at the accumulation time of 900 s), the simulated pseudopolarograms (using the parameters obtained by polarography: the formal potential, E° ; the diffusion coefficient, D ; the diffusion layer thickness, δ) match the experimental ones in a wide range of the accumulation potential. Difficulties in the data treatment of the reversible (pseudo)polarograms are rarely encountered. Logarithmic analysis is a common test of the reversibility of the polarographic curves. A linear relationship with a slope of 0.0591/ n indicates a reversible system. However, it is important to emphasize that the curve of the logarithmic analysis of reversible pseudopolarograms is not linear in the whole potential range, as compared with the polarographic case. As shown in the inset in Fig. 5(a), in the region of the half-wave potential, the slope of the curve is about 20% higher

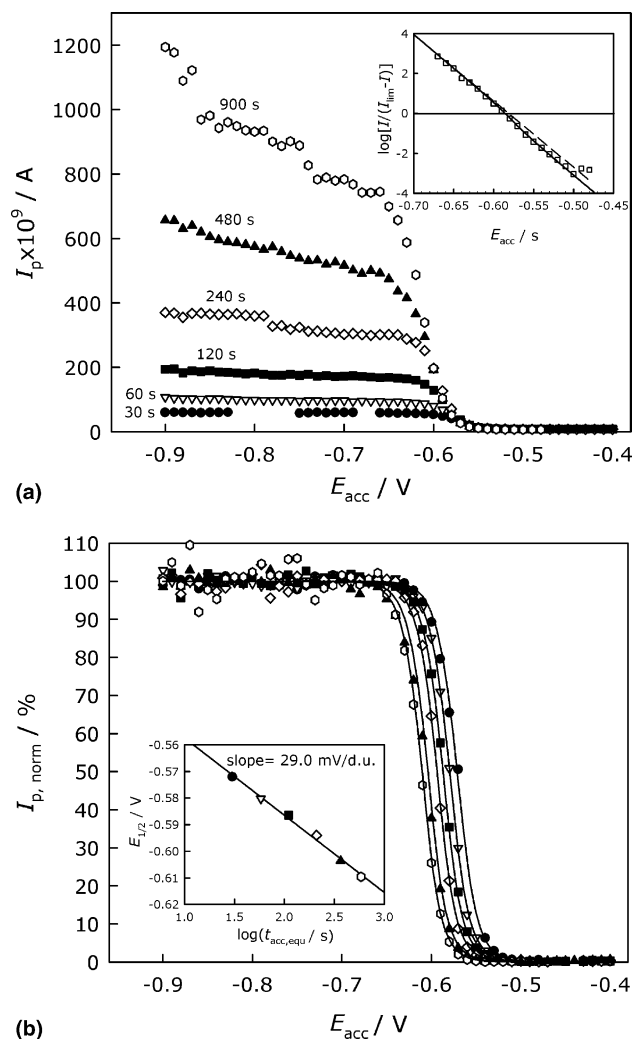


Fig. 5. The original (a) and normalized (b) pseudopolarograms of 1×10^{-7} mol dm⁻³ Cd(II) in the supporting electrolyte of 0.1 mol dm⁻³ NaClO₄, pH <2, at different accumulation times (●, 30 s; ▽, 60 s; ■, 120 s; ◇, 240 s; ▲, 480 s; ○, 960 s). The full lines represent simulated pseudopolarograms. The DPASV parameters: $E_i = -0.75$ V, $E_f = -0.4$ V, $E_{st\ inc} = -0.002$ V, $E_A = 0.025$ V, $t_{int} = 0.2$ s, $t_{mod} = 0.05$ s. The simulation parameters: $\delta = 1.0 \times 10^{-3}$ cm, $D = 0.52 \times 10^{-5}$ cm² s⁻¹, $E_{form} = -0.553$ V, $r_{drop} = 0.0351$ cm. Insets: (a) the logarithmic analysis of the experimental pseudopolarogram of Cd(II) obtained at $t_{acc} = 120$ s (symbols); full line represents simulated pseudopolarogram, and dashed line is straight line with reversible slope. (b) the dependence of the half-wave potential of the pseudopolarograms on the logarithm of the equivalent accumulation time.

prior to and after this section, indicating “higher” reversibility with a reciprocal slope of 24.5 mV, as compared with the expected 29.5 mV in other segments of the pseudopolarograms (assuming two-electron charge transfer). Such an increased slope, proposed by the theory for a HMDE [4], was also obtained for both the theoretical and the experimental scanned stripping chronopotentiometric (SSCP) curves [12]. The slope re-

mains unaffected by the metal complexation, until the electrochemical reactions (pseudo/polarograms) become reversible (with an unchanged diffusion coefficient of the electroactive species [13]). Therefore, the corresponding reversible half-wave potential can be used for the metal complexation studies. However, a different approach must be considered for the quasireversible and the irreversible electrochemical reactions.

3.3. Quasireversible electrochemical system

A typical example of the quasireversible system is the electrochemical reaction of zinc(II) in a supporting electrolyte of higher ionic strength (over 1 mol dm⁻³) [15–17,32,33]. The reaction is reversible at lower ionic strengths (e.g., 0.1 mol dm⁻³).

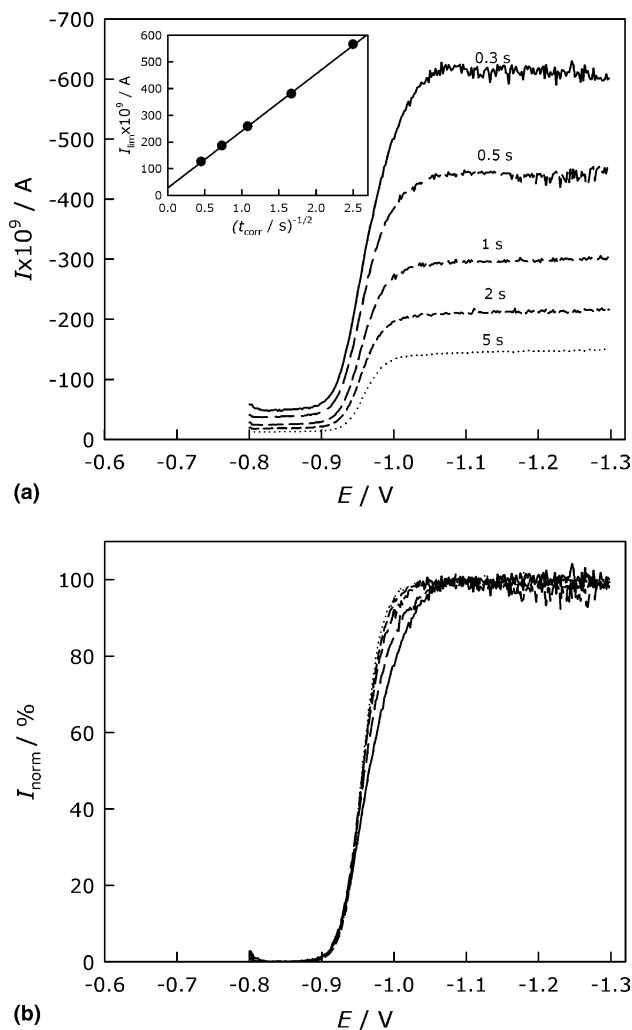


Fig. 6. The original (a) and normalized (b) sampled dc polarograms of 1×10^{-4} mol dm⁻³ Zn(II) in the supporting electrolyte of 1 mol L⁻¹ NaClO₄, pH 4.7 ± 0.1 , at different “times between drop”. Inset: The dependence of the limiting current on the reciprocal value of the square root of the corrected drop time.

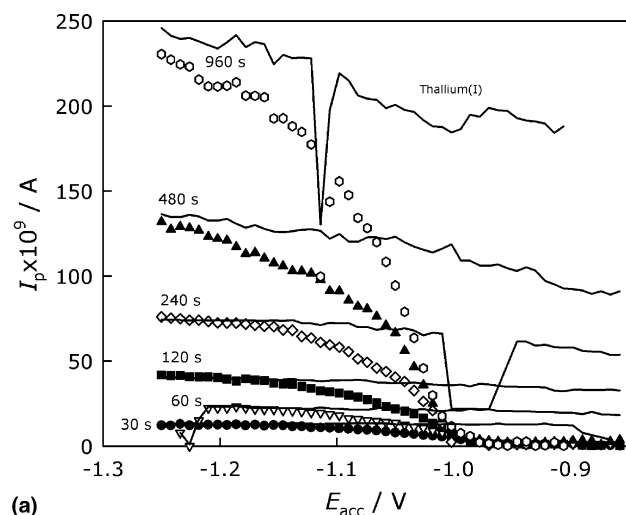
The measurements were performed in 1 mol dm⁻³ NaClO₄ at pH 4.7 ± 0.1 (an acetate buffer). The polarographic measurements of zinc(II) were also performed for comparison. Fig. 6 shows the original (a) and the normalized (b) polarograms of a 1×10^{-4} mol dm⁻³ Zn(II) at various drop times. The shift of the half-wave potential to more positive potentials with increasing drop-time is in good agreement with the theoretical proposal. The change of the shape is more significant in the upper part of the polarograms (above 40%). Using a corrected drop time [18], a linear relationship of the limiting current on the reciprocal value of the square root of the drop time was obtained (inset in Fig. 6(a)). Table 1 presents the formal potential (E°/V), the transfer coefficient (α) and the rate constant ($k_s/\text{cm s}^{-1}$) obtained by comparing the experimental and the simulated polarograms. These values are in good agreement with the literature data [32,33].

The pseudopolarographic measurements were performed in the same electrolyte solution with 5×10^{-8} mol dm⁻³ Zn(II). The shape of the limiting currents of the pseudopolarograms can be changed considerably, as described elsewhere [18]. This problem can be solved graphically/mathematically [18], or by using the additional redox process as an internal standard [28]. The latter was useful when the potentials of the redox reaction of the metal investigated, and an internal standard were separated enough. Tl(I) was used as a real internal standard because of the well-separated potentials of the redox reactions of Tl(I) and Zn(II). A concentration of 1×10^{-7} mol dm⁻³ Tl(I) was selected in order to produce similar currents to those in 5×10^{-8} mol dm⁻³ Zn(II). Fig. 7 illustrates the pseudopolarograms of Zn(II) (points) and Tl(I) (lines) obtained with increasing accumulation times. It is evident that the limiting currents of the pseudopolarograms of both redox processes are not constant. A possible explanation of such behavior of the limiting currents is given elsewhere [9,10,18,34,35]. The normalization of the pseudopolarograms of Zn(II) was performed as described previously [18], and is presented in Fig. 7(b). The half-wave potential of the pseudopolarograms shifts to more negative potentials with increasing accumulation time, but to a lesser extent in comparison with the reversible pseudo-

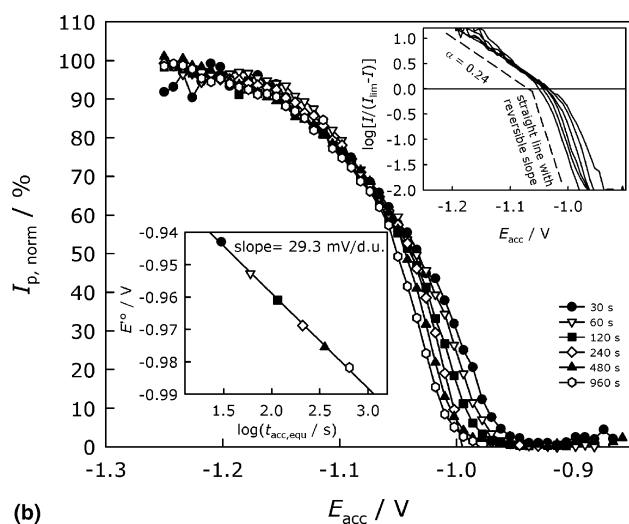
Table 1

The formal potential (E°/V), the rate constant ($k_s/\text{cm s}^{-1}$) and the transfer coefficient (α) of the electrochemical reaction of Zn(II) in a 0.1 mol dm⁻³ NaClO₄, pH 4.7 ± 0.1 at various mercury drop time determined by comparing experimental and simulated polarograms

t_{drop}/s	E°/V	$10^3 k_s/\text{cm s}^{-1}$	α
0.3	-0.964	3.2	0.26
0.5	-0.964	3.0	0.24
1	-0.965	3.0	0.24
2	-0.966	3.0	0.24
5	-0.966	3.0	0.24



(a)



(b)

Fig. 7. The original (a) and normalized (b) experimental pseudopolarograms of $5 \times 10^{-8} \text{ mol dm}^{-3}$ Zn(II) (symbols) and $1 \times 10^{-7} \text{ mol dm}^{-3}$ Tl(I) (lines) in the supporting electrolyte of 1 mol dm^{-3} NaCl, pH 4.7 ± 0.1 , at different accumulation times (●, 30 s; ▽, 60 s; ■, 120 s; ◇, 240 s; ▲, 480 s; ○, 960 s). The DPASV parameters: $E_i = -1.1 \text{ V}$, $E_f = -0.20 \text{ V}$, $E_{st \text{ inc}} = -0.002 \text{ V}$, $E_A = 0.025 \text{ V}$, $t_{int} = 0.2 \text{ s}$, $t_{mod} = 0.05 \text{ s}$. Insets in (b): upper – the logarithmic analysis of the pseudopolarograms of Zn(II); lower – the dependence of the formal potential on the logarithm of the equivalent accumulation time.

polarograms. As shown in Fig. 3(b), the range where the slope of the pseudopolarographic curve is reversible, expands to a higher percentage of the limiting current with increasing accumulation time. It has been estimated that such a range for the experimental pseudopolarograms of Zn(II) varies from 5% at $t_{acc} = 30 \text{ s}$ to 15% at $t_{acc} = 960 \text{ s}$. It is well defined for all the pseudopolarograms and enables the determination of the formal potential (E^o/V), the transfer coefficient (α) and the rate constant ($k_s/\text{cm s}^{-1}$) for the electrochemical reaction of Zn(II)/Zn(0). These data were obtained by comparing the experimental and the simulated pseudopolarograms (Table 2). Slightly different values in comparison with

Table 2

The formal potential (E^o/V), the rate constant ($k_s/\text{cm s}^{-1}$) and the transfer coefficient (α) of the electrochemical reaction of Zn(II) in 0.1 mol dm^{-3} NaClO₄, pH 4.7 ± 0.1 at various accumulation time determined by comparing experimental and simulated pseudopolarograms

t_{acc}/s	E^o/V	$k_s/\text{cm s}^{-1}$	α
30	-0.970	2.1	0.24
60	-0.970	2.2	0.25
120	-0.970	2.2	0.23
240	-0.970	2.2	0.24
480	-0.970	2.3	0.23
960	-0.970	2.2	0.23

the polarographic data were obtained. The formal potential is more negative (about 4 mV), the rate constant is about 30% lower, while the transfer coefficients are equal. Although the pseudopolarograms were normalized using the internal standard method, these differences probably occur as a consequence of a non-ideal form of the pseudopolarograms and the mathematical treatment used.

The logarithmic analysis of the pseudopolarograms of Zn(II) is illustrated in the inset of Fig. 7(b). The main distinction between the logarithmic curves is mostly in the lower part ($\log[I/(I_d - I)] < 0.2$). All the curves in the upper part have the same slope, whence the transfer coefficient of 0.24 ± 0.02 was calculated and found to be equal to the transfer coefficients presented in Table 2.

A logarithmic analysis is a suitable test for the polarographic measurements of the reversibility system. Besides, these curves also allow the determination of the transfer coefficient. Fig. 8 shows a logarithmic analysis of the simulated sampled dc polarograms (a) and pseudopolarograms (b) for the reversible (curves 1), quasireversible (curves 2) and irreversible (curves 3) systems. The slope of the curve of the logarithmic analysis obtained for the reversible systems is $0.0591/n$, where n is the number of electrons exchanged. The transfer coefficient (α) for the non-reversible systems can be evaluated from the expression $(0.0591/\alpha n)$. Depending on the simulated parameters, a curve with a varying slope is obtained. The slope of the logarithmic curve is reversible both in the lower and in the upper part. The slope of the curve in the middle is influenced by the transfer coefficient. However, Fig. 8(a) clearly shows that such a slope is obtained for the irreversible system only (curve 3). For the quasireversible system (curve 2), the estimated transfer coefficient ($\alpha = 0.73$) is almost 50% higher than that selected in the simulation ($\alpha = 0.5$). For the irreversible system (curve 3), there is relatively a wide range of the slopes of the curves where the calculated transfer coefficient is equivalent to the simulated one ($\alpha = 0.5$). It is obvious that the logarithmic analysis is an unsuitable method for the determination of the transfer coefficient for the quasireversible systems using polarographic curves.

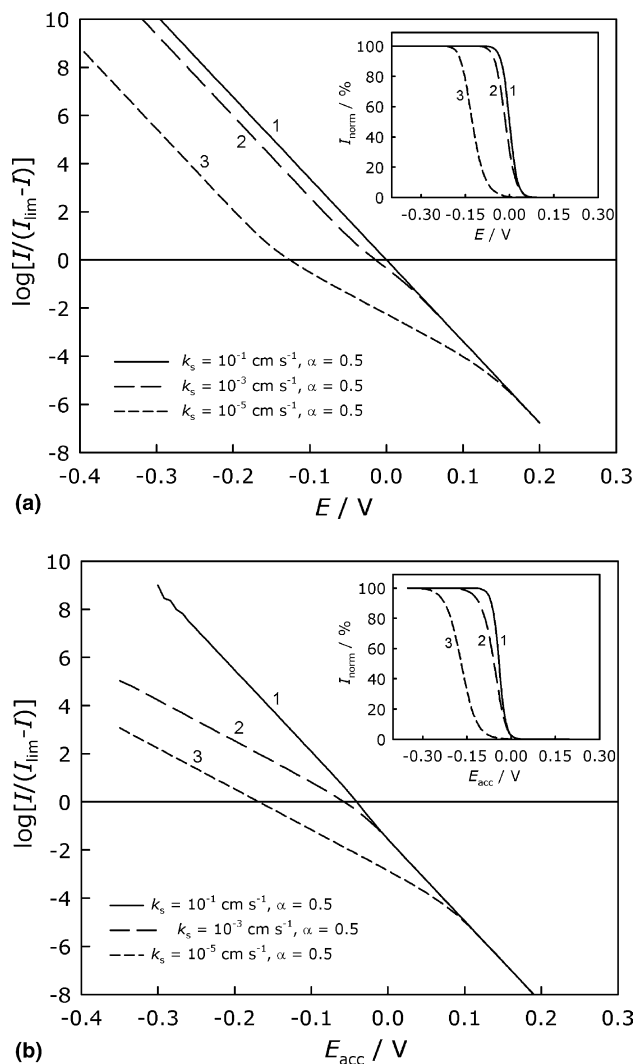


Fig. 8. The logarithmic analysis of the simulated reversible, quasireversible and irreversible polarograms (a) and pseudopolarograms (b) for two-electron charge transfer. Simulation parameters: (a) $t_{\text{drop}} = 1$ s, $D = 1 \times 10^{-5}$ cm² s⁻¹, $E_{\text{form}} = 0$ V; (b) $t_{\text{acc}} = 60$ s, $\delta = 1.4 \times 10^{-3}$ cm, $D = 1 \times 10^{-5}$ cm² s⁻¹, $E_{\text{form}} = 0$ V, $r_{\text{drop}} = 0.0351$ cm. Insets: Corresponding polarograms/pseudopolarograms.

The pseudopolarographic curves behave in a different manner. Fig. 8(b) clearly illustrates that only two slopes are visible on the logarithmic curves for both rate constants: the reversible slope in the lower part of the curve and the quasireversible/irreversible slope with a calculated transfer coefficient which is equal to the simulated one ($\alpha = 0.5$). The polarographic and the pseudopolarographic measurements of the quasireversible electrochemical reactions of Zn(II) in 1 mol dm⁻³ NaClO₄ confirmed such behavior of the logarithmic curves (Fig. 9). The logarithmic analysis of the (pseudo)polarograms of Zn(II) evidently shows a different slope in the upper part of the log-curves. The transfer coefficient calculated from the logarithmic curve of the polarograms is $\alpha = 0.62$, which is 2.5 times higher than the

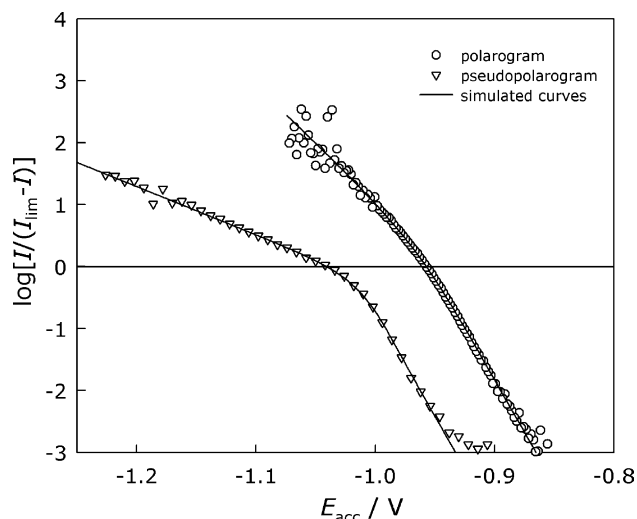


Fig. 9. The logarithmic analysis of the experimental (symbols) and simulated (lines) polarogram (\circ , $t_{\text{drop}} = 1$ s) and pseudopolarogram (∇ , $t_{\text{acc}} = 120$ s) of Zn(II). The original polarogram and pseudopolarogram are presented in Figs. 6 and 7, respectively.

transfer coefficient estimated by comparing the experimental and the simulated polarograms ($\alpha = 0.25$). However, the transfer coefficient calculated from the logarithmic curve of the pseudopolarogram is in good agreement with the transfer coefficient estimated by comparing the experimental and the simulated pseudopolarograms ($\alpha = 0.24$).

3.4. Irreversible electrochemical system

The redox reaction of the cadmium–nitrilotriacetate complex (CdNTA) served as an example for the studies of the pseudopolarographic characteristics of the irreversible electrochemical systems. The CdNTA is a chemically stable complex ($\log K = 9.76$, at $\mu = 0.1$ mol dm⁻³) which is irreversibly reduced at a more negative potential (about 350 mV) ($E_{1/2, \text{irrev}} \sim -0.9$ V) as compared with the reduction of the free/labile complexed Cd(II) ($E_{1/2, \text{rev}} \sim -0.55$ V) [28]. The standard rate constant (about 1×10^{-4} cm s⁻¹) and the transfer coefficient ($\alpha = 0.5$ – 0.6) for this electrochemical reaction have been published elsewhere [28].

All measurements were performed in the electrolyte solution consisting of 0.1 mol dm⁻³ NaClO₄, at pH 7.9 ± 0.1 (buffered with a 5×10^{-3} mol dm⁻³ borate buffer). In all experiments, NTA was added to the solution so that more than 95% of Cd(II) would be complexed.

The polarographic measurements of the CdNTA were also performed for comparison. Fig. 10(a) illustrates the polarograms of the CdNTA complex (1×10^{-4} mol dm⁻³ Cd(II) + 2×10^{-4} mol dm⁻³ NTA) measured at various drop times. The limiting current of the polarograms decreased with an increase of the mercury

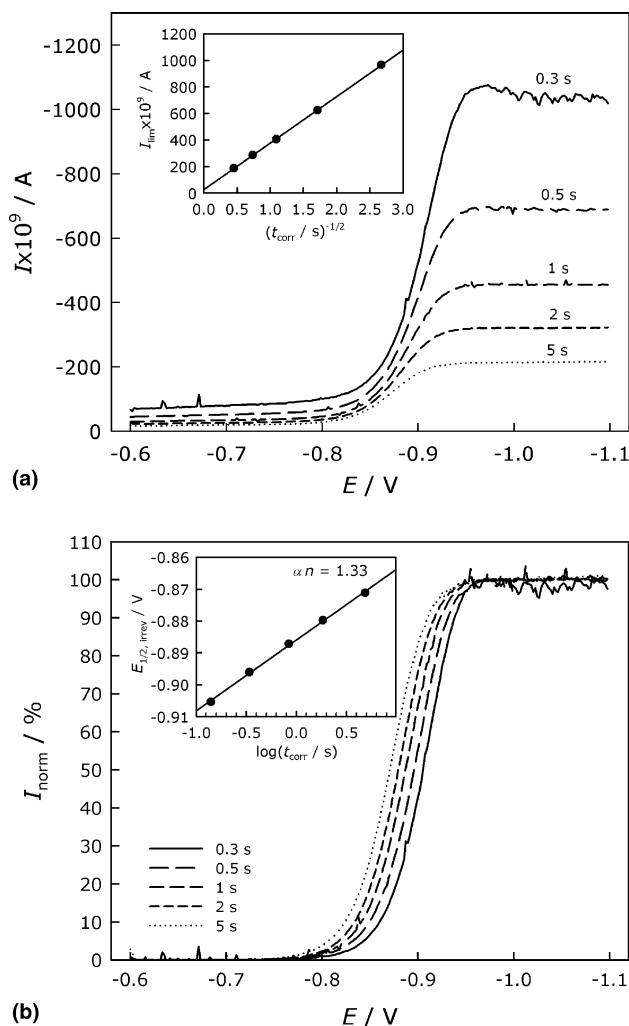


Fig. 10. The original (a) and normalized (b) sampled dc polarograms recorded in the supporting electrolyte of $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$, pH 7.9 ± 0.1 at a total concentration of $1 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cd(II)}$ and $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ NTA}$ at different “times between drop”. Inset: (a) The dependence of the limiting current on the reciprocal value of the square root of the corrected drop time. (b) The dependence of the irreversible half-wave potential on the logarithm of the corrected drop time.

drop time, giving a linear relationship with the inverse square root of the corrected drop time [18], and indicating the diffusion-controlled electrochemical reaction. The characteristic shift of the half-wave potential of the polarograms to positive values with increasing drop time is illustrated in Fig. 10(b), where the normalized polarograms are plotted. Using Eq. (1) [36]

$$\Delta E_{1/2, \text{irr}} / \log(t_{\text{drop}}) = 0.0295 \text{ V} / \alpha n, \quad (1)$$

the transfer coefficient is calculated as $\alpha = 0.66$ (inset in Fig 10(b)). However, the transfer coefficient of 0.54 (which is closer to the literature data) is estimated by comparing the experimental and the simulated polarograms. As pointed out in Section 3.1, by establishing the reversible part of the polarograms, it is possible to de-

termine a formal potential, which is essential in determining the rate constant. The lower limit for the precise estimate of the reversible part of the experimental curves is about 1%. Because of the baseline deviation in the lower part of the polarograms, it was impossible to determine the reversible part of the polarograms accurately. However, the slope at the foot of the polarograms tends to be reversible which gives an estimated formal potential of $E^\circ = -0.835 \pm 0.010 \text{ V}$. Consequently, a rate constant of $k_s = 1.0 \pm 0.4 \times 10^{-4} \text{ cm s}^{-1}$ and a transfer coefficient of $\alpha = 0.54$ are evaluated. These values are in accordance with the literature data [28].

The results of the pseudopolarographic measurements of the CdNTA complex are illustrated in Figs. 11(a) and (b). The total concentrations of $1 \times 10^{-7} \text{ mol dm}^{-3} \text{ Cd(II)}$ and $3 \times 10^{-6} \text{ mol dm}^{-3} \text{ NTA}$ were added to $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ of the supporting electrolyte solution. The pH of the solution was adjusted with a borate buffer to 7.9 ± 0.1 . Under these conditions, more than 95% of Cd(II) is complexed with NTA. The basic principle of the anodic stripping voltammetry of the inert complexes is a reduction of the complex at potentials more negative (mostly by more than 100 mV) than the reduction potential of the free/labile metal complexes. In the reverse process, the amalgamated metal oxidizes to the free/labile metal ions. The chemical reaction of the inert complex formation with a ligand present in the solution follows the redox process.

As pointed out in recent publications [18,21,37], an adequate treatment of the voltammetric curves (primary data) is the key to obtaining the representative secondary data [37] (e.g., pseudopolarogram) which accurately interpret the electrochemical reaction investigated. The change in the shape of the voltamograms indicates a potential additional process which coincides with the oxidation. The anodic voltamograms, obtained under our experimental conditions, were asymmetrical, which is typical for simple systems. The normalized voltamograms for different accumulation times (accumulated at $E_{\text{acc}} = -1.25 \text{ V}$) illustrate such behavior (inset in Fig. 11b). At an accumulation time of 30 s, only one peak with a very small shoulder at the positive side of the peak was observed. However, with an increase of the accumulation time, the main peak shifted to more positive values, its peak potential being equal to the position of the small shoulder visible at $t_{\text{acc}} = 30 \text{ s}$. The pre-peak (shoulder) at the left side of the peak has the same position as the main peak at $t_{\text{acc}} = 30 \text{ s}$. It is obvious that the pre-peak becomes relatively smaller with an increase of the accumulation time, but its absolute value remains unchanged. The selected measurements showed that such a pre-peak appeared only in the system where both Cd(II) and NTA were present in the solution, with an excess of NTA over Cd(II).

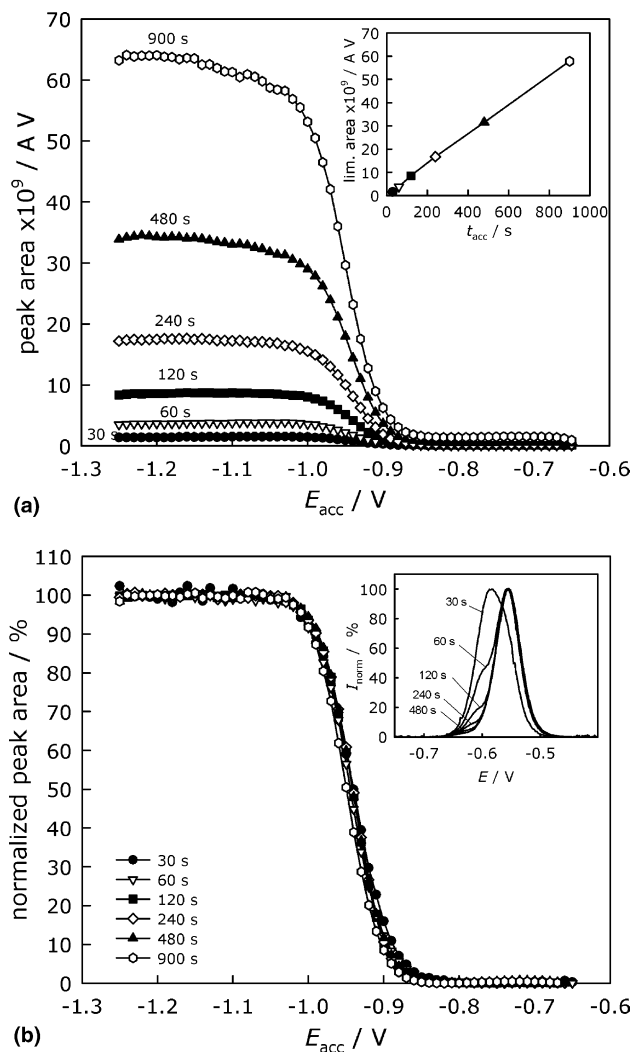


Fig. 11. The original (a) and normalized (b) pseudopolarograms (constructed as peak area vs. accumulation potential) recorded in the supporting electrolyte of $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$, $\text{pH } 7.9 \pm 0.1$ at a total concentration of $1 \times 10^{-7} \text{ mol dm}^{-3} \text{ Cd(II)}$ and $3 \times 10^{-6} \text{ mol dm}^{-3} \text{ NTA}$ at different accumulation times (\bullet), 30 s; (∇), 60 s; (\blacksquare), 120 s; (\diamond), 240 s; (\blacktriangle), 480 s; (\circ), 900 s. The DPASV parameters: $E_i = -0.75 \text{ V}$, $E_f = -0.40 \text{ V}$, $E_{st \text{ inc}} = -0.002 \text{ V}$, $E_A = 0.025 \text{ V}$, $t_{int} = 0.2 \text{ s}$, $t_{mod} = 0.05 \text{ s}$. Inset: (a) The dependence of the limiting current on the accumulation time. (b) The normalized anodic voltammograms of cadmium recorded at different accumulation times and at an accumulation potential of $E_{acc} = -1.25 \text{ V}$. The normalization is carried out by dividing the current of the voltammogram with its peak current (I/I_p).

The differential pulse voltammetry was used as a scanning technique for the pseudopolarographic measurements. According to the abovementioned, the sequence of the electrochemical processes at the surface of the mercury drop electrode which causes the appearance of the double peaks, can be reconstructed. The application of the positive potential pulse during the anodic stripping scan results in Cd(Hg) being oxidized to Cd^{2+} , after which the complexation (with an excess of NTA) takes place in the vicinity of the electrode surface. After ending the potential pulse, the CdNTA complex formed

is not reduced back to Cd(Hg), because the actual scanning potential is more positive (about 0.3 V) than the potential of the CdNTA reduction. This cycle is repeated for each potential step, until the excess of NTA in the vicinity of the electrode surface is used for the complexation of the Cd^{2+} ions formed. This process diminishes the concentration of the Cd(Hg) in each potential step much more than in the absence of the complexation. Afterwards, the oxidation of the Cd(Hg) proceeds without the complexation of Cd^{2+} with NTA. The concentration of the accumulated amalgam increases with the accumulation time, causing the main peak to become higher, while the negative peak (shoulder) remains practically unchanged (its relative value diminishes). The position of the negative peak (shoulder) is more negative (by about 50 mV), as compared with the main peak, which is probably caused by the kinetic lability of the CdNTA complex formed under these experimental conditions.

Since pseudopolarography is a method in which the reduction is the major process, and the oxidation is only its reverse, it is necessary to construct the pseudopolarograms from the values corresponding to the reduction process. An appropriate method is to use the peak area instead of the peak current [21]. Therefore, the pseudopolarograms illustrated in Fig. 11 are constructed in this manner. Although the form of the anodic voltammograms was changed by the excess of NTA, the shape of the pseudopolarograms (constructed from the peak area) was not significantly affected. Subsequently, it is assumed that these pseudopolarograms accurately reflect the nature of the irreversible electrochemical reactions of the CdNTA complex. As expected, the half-wave potential ($E_{1/2, irr} = -0.940 \text{ V}$) did not change with the accumulation time. A small difference between the pseudopolarograms (about 5 mV) may be a consequence of the data treatment and/or the variation of the reference electrode potential over about 35 h of continuous measurements. The logarithmic analysis of all pseudopolarograms yields a transfer coefficient between 0.5 and 0.6, as estimated by comparing the experimental and the simulated pseudopolarograms. However, as far as the polarographic data were concerned, it was impossible to resolve the reversible part of the pseudopolarograms, necessary for the estimation of the formal potential, and subsequently the rate constant. However, using the electrochemical parameters estimated by polarography, ($E^{o'} = -0.835 \text{ V}$, $k_s = 1 \times 10^{-4} \text{ cm s}^{-1}$ and $\alpha = 0.54$), the simulated pseudopolarographic curves obtained matched the experimental ones.

Pseudopolarographic measurements performed with varying accumulation times can be helpful in making a distinction between irreversible processes (with two-electron charge transfer and no change of the half-wave potential) and reversible processes (with one-electron charge transfer and a shift of the half-wave potential).

4. Conclusions

The main parameters in the trace metal speciation studies using electrochemical/voltammetric methods are the potential of the redox reaction and the amplitude of the corresponding signal, which are dependent on the technique applied and the experimental conditions. Major physico-chemical processes which affect the variation of these parameters are: the change of the distribution of metal species due to the change of the electrolyte composition, the change of the conditions on the electrode surface (e.g., adsorption/desorption processes) and the reversibility of the electrochemical reaction. It is very important to resolve the main problem which causes the change of these parameters. Depending on the technique used, for the polarographic/voltammetric measurements, a change of both the redox potential and the amplitude of the corresponding signal with the change of the reversibility of the electrochemical reaction can be expected.

The pseudopolarography is a unique, very sensitive voltammetric method capable of direct measurements of the main group of trace metal species (labile and inert complexes) at very low concentration levels, i.e., in natural waters. The shape of the pseudopolarographic curve is affected by two processes: (1) the accumulation (reduction) of the metal and (2) the oxidation of the accumulated metal (applying the voltammetric/potentiometric technique). Therefore, different theoretical models, taking into account both steps (accumulation and oxidation/stripping), can be helpful in understanding the experimental pseudopolarographic curves.

This paper describes the main characteristics of the pseudopolarographic curves representing the reversible, quasireversible and irreversible electrochemical reaction, which have not so far been well documented experimentally.

All experimentally obtained curves are in good agreement with the theoretically calculated ones. A proper data treatment, starting with the determination of a peak current/area to the normalization of the constructed pseudopolarographic curve, is achieved enabling a reliable determination of the electrochemical parameters.

The simulated reversible, quasireversible and irreversible pseudopolarographic curves show that there is a range at the foot of the curves with a reversible character. By finding this range for the experimental curves, the determination of the parameters of the electrochemical reaction becomes possible. By changing the setup of the experiment (accumulation time, mercury drop size, intensity of stirring), this measurable “reversible” range can be extended to a higher percentage of the total current, allowing its reliable determination. The minimal value achieved experimentally is about 1%, which corresponds to the electrochemical reaction with $\alpha \sim 0.5$ and $k_s \geq 10^{-4} \text{ cm s}^{-1}$.

The original pseudopolarographic curves are constructed as anodic peak current versus accumulation potential. In this case, the anodic peak current is the anodic “measure” of the reduction process of the accumulated metals only. Accordingly, as the “measure” of the reduction process, other characteristics of the anodic signal can be used (e.g., peak area, stripping time in potentiometry). Generally, it is recommended to use a signal characteristic which is better related to the reduction process. Besides, in some cases when the electrochemical reaction becomes more complex due to the additional processes at the electrode surface (adsorption), a suitable scanning technique (e.g., sampled dc) yields more appropriate results [12,13,21].

Logarithmic analysis of the quasireversible polarographic curves is unsuitable for the determination of the transfer coefficient. However, accurate values for the transfer coefficient can be obtained from the logarithmic analysis of the pseudopolarographic curves.

Although the logarithmic curve of reversible pseudopolarograms is not linear in the whole potential range (as is common for the polarographic curves), the speciation of trace metals (e.g., using the DeFord–Hume approach for the labile complexes) remains unaffected unless the reversibility of the electrochemical reaction is not changed.

The change of the diffusion coefficients of the metal species will be discussed in detail in further elaboration on the practical application of pseudopolarography for the speciation of labile and inert metal complexes.

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