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Original Scientific Paper

Pseudopolarography of Trace Metals. Part III. Determination of Stability Constants of Labile Metal Complexes*

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Suitability of the pseudopolarographic approach for determination of the stability constants of labile metal complexes at low metal concentrations is explored. It is shown that the methodology based on the DeFord-Hume principle can be successfully applied to treat data obtained from pseudopolarograms. For reversible electrochemical systems, such as thallium(I)–chloride or cadmium(II)–chloride, the half-wave potential of a pseudopolarogram, or the corresponding "critical" potential, can be used to calculate the stability constants. A "formal" potential, evaluated by manual fitting of experimental and simulated (pseudo)polarograms, or a potential in a range where all curves yield a reversible slope, can be used as the "critical" potential. For systems in which reversibility of the electrochemical reaction changes (zinc(II)–oxalate and bismuth(III)–chloride), the shift of the half-wave potential depends both on the complexation parameters and on reversibility of the electrochemical reaction. Therefore, in such cases only the "critical" potential can be used for determination of stability constants. All calculated stability constants presented in the paper are in good agreement with the literature values. The benefit of using pseudopolarographic approach lies in the minimization of various effects (such as precipitation, adsorption, ligand excess, *etc.*), which can influence determination of stability constants at higher metal concentrations.

Keywords
pseudopolarography
metal speciation
stripping voltammetry
stability constants

INTRODUCTION

Speciation of trace metals in natural waters is of great interest because the interaction of metals with living organisms and nonliving particles depends on their species.[1–5] These determinations become very complicated at low metal concentrations in natural waters. The most advantageous approach for trace metals speciation is based on the utilization of methods that enable measurements at natural level concentrations.[6] Results obtained from the measured data, such as stability constants of metal complexes, are representative of given natural conditions, whether expressed as conditional, concentration or thermodynamic values.[7–9] It has been shown that electrochemical stripping techniques (anodic and cathodic stripping voltammetry, potentiometric stripping) generally meet the required criteria of sensitivity and selectivity.[4,5,10,11] Pseudopolarography (originally based on ASV) is the electroanalytical method suitable for metal speciation at its natural concentrations.[12–15] The simplest contribution of pseudopolarography is the distinction between labile and inert metal complexes.[16–17] Additional benefit of pseudopolarography in trace metal complex studies (*e.g.,* determination of stability constants), is avoidance

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* Dedicated to the memory of the late Professor Marko Branica.

of problems connected with high metal concentrations (such as precipitation, sufficient ligand excess, *etc.*). Moreover, the concentration ratio of all elements in the sample approaches their natural values, and side reactions involved in the data treatment are mostly negligible.

Pseudopolarography can be successfully applied for speciation studies of labile and inert metal complexes.[9,12–29] It has been shown that the DeFord-Hume method,[30] used for determination of stability constants, is applicable to reversible[12–14,18–22] and quasireversible[24–27] electrochemical systems. This original approach is valid only for systems in which the rate constant (k^o) is not changed by the ligand titration. However, the reversibility of some electrochemical reactions changes with the solution composition, and the DeFord-Hume expression based on half-wave potentials is not appropriate for stability constant calculations. Two possible ways to overcome this problem are: (i) calculation of reversible half-wave potential (knowing the rate constant k^o and standard (or formal) potential E^o of the electrochemical reaction), or (ii) determination of potentials at the foot of the (pseudo)polarographic curve, where the curve yields a reversible slope ("critical" potential). The latter is a simpler approach, but its application is limited if a non-ideal baseline and current noise are present. In such cases, appropriate treatment of the (pseudo)polarographic curve has a crucial role.[31] As previously demonstrated, the shape of the pseudopolarographic wave mostly depends on deposition time.[32] For reversible electrochemical reactions, only a shift of the whole pseudopolarogram to more negative potentials is observed with increasing deposition time, without any change of its shape. However, quasireversible pseudopolarograms change both their shape and position, while irreversible pseudopolarograms are virtually independent on deposition time.[32] The main difference occurs at the foot of the quasireversible and irreversible pseudopolarographic curves. By increasing the deposition time, this lower part of the curve assumes a reversible shape. It was estimated that for irreversible pseudopolarograms with k^o about 10^{-4} cm s^{-1}, this reversible part can be extended to about 1 % of a total curve.

In recent years, a new method analogous to pseudopolarography, stripping chronopotentiometry at scanned deposition potential (SSCP), was developed.[33–38] Similar characteristics of reversible, quasireversible and irreversible curves obtained by the SSCP method are illustrated. In a series of publications, Town and van Leeuwen showed the advantage of using such an approach in speciation of trace metals.[33–38] For some specific conditions (*e.g.*, metal-ligand ratio, adsorption effects), stripping chronopotentiometry showed an advantage over the classical stripping voltammetric technique.[36–39]

These features of SSCP and pseudopolarographic curves can be utilized in trace metal speciation at low metal concentrations as criteria in distinguishing the reversibility of the electrochemical reaction from the heterogeneity of the sample.

In this work, pseudopolarographic determination of stability constants of labile metal complexes at low metal concentrations is verified. The basic principle of the DeFord-Hume method is tested on two simple reversible systems (thallium(I) chloro and cadmium(II) chloro complexes). The same approach is extended to systems with variable reversibility of the electrochemical reaction (zinc(II) oxalato and bismuth(III) chloro complexes).

Simulated pseudopolarographic curves were obtained using the theory proposed by Shuman and Cromer.[15]

EXPERIMENTAL

Reagents

All solutions were prepared in deionized water from a Milipore Milli-Q system (Bedford, USA) using chemicals of "analytical-reagent" grade (NaCl, $NaClO_4 \cdot H_2O$ (Merck, Darmstadt), sodium oxalate (Kemika, Zagreb)) and "suprapure" (sodium acetate and concentrated $HClO_4$). Stock metal solutions (Cd, Tl, Zn, Bi) were prepared by dilution of commercial standards. A stock acetate buffer solution (3 M, pH = 4.7±0.1) was prepared by dissolving solid sodium acetate in Milli-Q water. Electrolyte solutions in the cell were initially purged by oxygen-free nitrogen for at least 15 minutes, followed by maintaining a nitrogen blanket above the electrolyte surface during measurements.

Instrumentation

All measurements were performed using a μ-Autolab potentiostat (EcoChemie, Utrecht, The Netherlands) in conjunction with either PAR 303A (middle drop size, 1.55 mm^2) or Metrohm 663 VA stand (small drop, 0.25 mm^2). The working electrode was a mercury drop electrode, the counter electrode was a platinum wire, and the reference electrode was Ag | AgCl (sat. NaCl). All measurements were performed at 22 ± 1 °C. pH was controlled by an Orion Research pH meter (EA 920) with a glass pH electrode.

Voltammetric Parameters

Differential pulse voltammetry (DPV) and sampled d.c. (in direct mode or as stripping, SDC) were used as scanning techniques under the selected conditions. For pseudopolarographic measurements, accumulation of metal ions was carried out during the deposition time (t_{dep}) at the selected range of deposition potential (E_{dep}). After the quiescent time, voltammetric scan was applied, starting from an initial (E_i) to a final potential (E_f), under the selected conditions of: differential pulse amplitude (A), potential step increment ($E_{st\ inc}$), time between pulses (t_{int}), and pulse duration (modulation) (t_{mod}) or drop time (t_d) (sampled d.c. polarography).

Automatic pseudopolarographic measurements were carried out using the newly developed software, PseudoSOFT. μ-AUTOLAB polarographic operations were controlled by the main programme module using a modified version of ElectroAnalytical System software, version 2.4 (EAS). This software enabled continuous experimental measurements for several days and the possibility of changing the supporting electrolyte composition by the use of an automatic burette system (Cavro, San Jose, USA).

RESULTS AND DISCUSSION

Simple Reversible Systems

Two simple model systems of labile complexes are used to test the methodology for determination of stability constants based on pseudopolarographic data. The first is a one-electron charge transfer model of thallium(I) chloro complexes and the second is a two-electron charge transfer model of cadmium(II) chloro complexes. For the reversible systems, both half-wave and the corresponding "critical" potential can be used for the stability constant calculation. In the case of thallium(I), the half-wave potential is used for the calculation, while the "critical" potential was utilized in the case of cadmium(II).

One-electron Charge Transfer

Thallium(I) forms relatively weak chloro complexes.[41,42] Due to a one-electron electrode reaction, a noticeable shift of the half-wave potential is expected. Determination of stability constants of 1×10^{-7} mol dm^{-3} Tl^{I} with chloride is performed at a constant ionic strength of 4 mol dm^{-3} with the composition (4–x) mol dm^{-3} $NaClO_4$ + x mol dm^{-3} NaCl (pH = 2).

Figure 1a shows normalized pseudopolarograms of Tl^{I} with increasing concentration of chloride. In the limiting current plateau of all pseudopolarograms, no significant change was observed (original curves are not presented). Thus, the term related to the change of diffusion coefficients $(0.059 \cdot \log(I_{ML}/I_M)/n)$[30] in expression (1), used for the stability constant calculation, was excluded. The shift of pseudopolarograms towards more negative potentials proves the formation of labile Tl^{I} chloro complexes. All pseudopolarograms are reversible, allowing calculation of stability constants by using the shift of the pseudopolarographic half-wave potential. Figure 1b shows the dependence of half-wave potential shifts (related to the half-wave potential without chloride) on chloride concentration. Stability constants are determined by fitting experimental points to the following model:[30]

$$\Delta E_{1/2}([\mathrm{X}]) = \frac{0.059}{n} \cdot \log(1+\beta_1 \cdot [\mathrm{X}] + \beta_2 \cdot [\mathrm{X}]^2 + \ldots + \beta_j \cdot [\mathrm{X}]^j), \quad (1)$$

where $\Delta E_{1/2}([\mathrm{X}])$ is the shift of half-wave potential, n is the number of exchanged electrons, [X] is the concentration of free ligand, β_j is the stability constant.

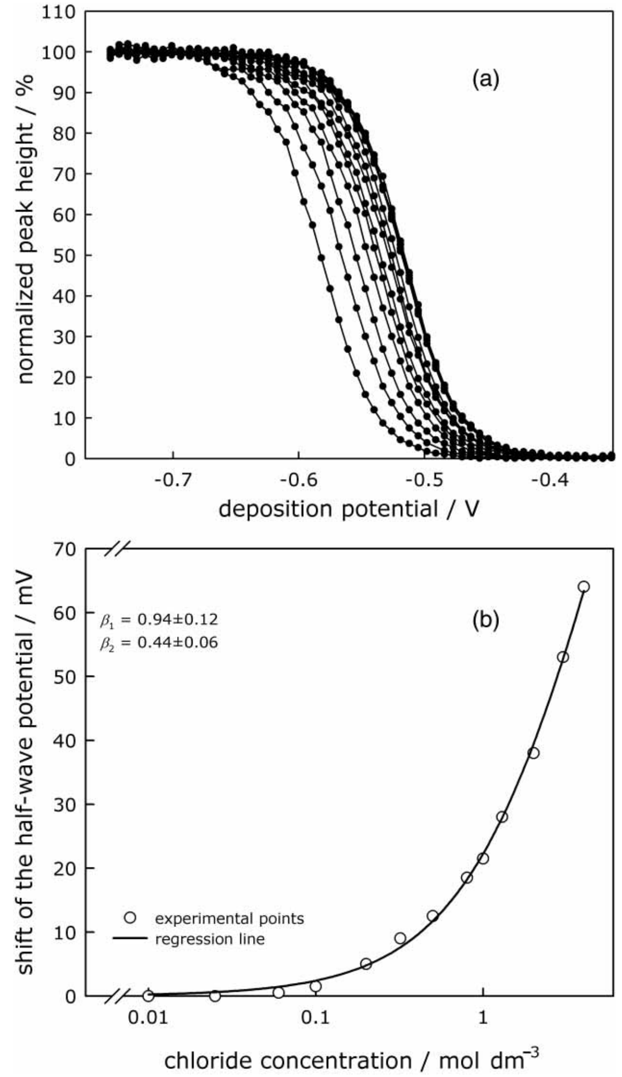

Figure 1. (a) Normalized pseudopolarograms of 1×10^{-7} mol dm^{-3} of Tl^{I} at constant ionic strength of 4 mol dm^{-3} [(4–x) mol dm^{-3} $NaClO_4$ + x mol dm^{-3} NaCl], at increasing concentration of chloride from 0 to 4 mol dm^{-3}. Instrument: μ-AUTOLAB, Electrode: modified PAR 303A, middle drop size. DPASV parameters: E_i = –0.65 to –0.75 V, E_f = –0.25 to –0.35 V, $E_{sc.inc.}$ = 0.002 V, A = 0.025 V, t_{dep} = 120 s, t_{int} = 0.2 s, t_{mod} = 0.05 s. (b) Dependence of the shift of the pseudopolarographic half-wave potential of Tl^{I} on chloride concentration.

The fitting is performed by the Marquardt-Levenberg numerical method assuming formation of one, two and three complex species. Statistical tests were applied to the obtained values, and the models with one ($\beta_1 = 1.81 \pm 0.35$) and three ($\beta_1 = 1.07 \pm 0.19$, $\beta_2 = 0.26 \pm 0.22$, $\beta_3 = 0.04 \pm 0.05$) complex species were discarded. The model with two complex species $[TlCl]^0$ and $[TlCl_2]^-$ was accepted with the following stability constants: $\beta_1 = 0.94 \pm 0.12$ and $\beta_2 = 0.44 \pm 0.06$. NIST critically selected stability constants of the metal ions database (ver. 5.0)[42] gives only the first stability constant for Tl^{I} at 4 mol dm^{-3} ionic strength (β_1 = 1). Database included in MINEQL+ software[43] gives two values valid only for zero ionic strength (β_1 = 4.786 and β_2 = 1.74), while for the same ionic strength NIST database reported the value of β_1 = 3.23. It is evident that various values of stability constants for Tl^I chloro complexes reported in literature are not consistent. Hence, our values are not comparable with the values obtained under different conditions.

Two-electron Charge Transfer

When compared to Tl^I chloro complexes, Cd^{II} forms stronger complexes with chloride.[42] Therefore, a greater shift of half-wave potential is expected, though the electrochemical reaction undergoes two-electron transfer. Measurements with cadmium were performed in the same way as for thallium(I) (1 × 10^{-7} mol dm^{-3} cadmium(II), 4 mol dm^{-3} ionic strength, (4–x) mol dm^{-3} $NaClO_4$ + x mol dm^{-3} NaCl (pH = 2)). The total number of recorded pseudopolarograms was 26, each consisting of 50 points (voltamograms), resulting in a total experiment duration of about 40 hours (60 s deposition time). Figure 2a shows all 26 normalized pseudopolarograms at different chloride concentrations. Each pseudopolarogram is compared to a simulated (reversible) pseudopolarogram to obtain a "critical/formal" potential, which is then used to investigate its dependence on the chloride concentration (Figure 2b). This "critical/formal" potential cannot be considered equivalent to a real formal potential since the diffusion layer thickness is unknown, which is a prerequisite for its accurate determination.

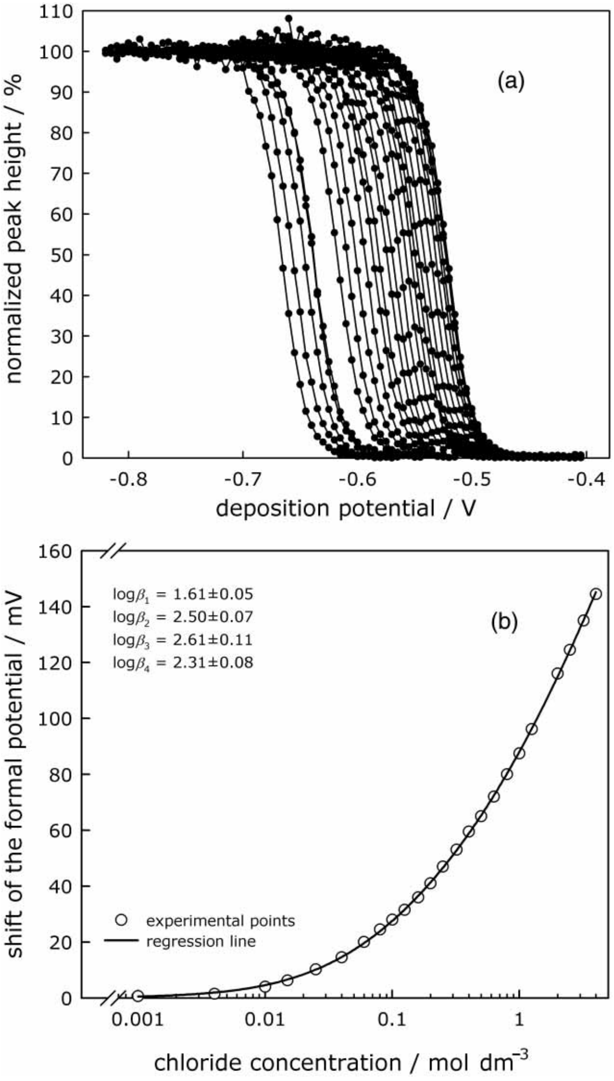

Figure 2. (a) Normalized pseudopolarograms of 1×10^{-7} mol dm^{-3} of Cd^{II} at constant ionic strength of 4 mol dm^{-3} [(4–x) mol dm^3 $NaClO_4$ + x mol dm^{-3} NaCl], at increasing concentration of chloride from 0 to 4 mol dm^{-3}. Instrument: μ-AUTOLAB, Electrode: modified PAR 303A, middle drop size. DPASV parameters: E_i = –0.65 to –0.80 V, E_f = –0.35 to –0.50 V, $E_{sc.inc.}$ = 0.002 V, A = 0.025 V, t_{dep} = 60 s, t_{int} = 0.2 s, t_{mod} = 0.05 s. (b) Dependence of the shift of the pseudopolarographic half-wave potential of Cd^{II} on chloride concentration.

TABLE I. Stability constants of Cd^{II} chloro complexes at 4 mol dm^{-3} ionic strength

	This work	Lit. 1[41]	Lit. 2[42]
log β_1	1.61 ± 0.05	1.66 ± 0.10	1.66 ± 0.10
log β_2	2.50 ± 0.07	2.40 ± 0.10	2.40 ± 0.10
log β_3	2.61 ± 0.11	2.80 ± 0.30	2.80 ± 0.30
log β_4	2.31 ± 0.08	2.20 ± 0.30	

Stability constants are calculated in the same way as for Tl^I. By using statistical tests, the formation of four chloro complexes with Cd^{II} ions at 4 mol dm^{-3} ionic strength is confirmed, and the resulting stability constants are given in Table I. Statistical tests rejected stability constants obtained by fitting experimental data to the model with three or five chloro complexes. The existence of three and four stability constantans of Cd^{II} chloro complexes is registered in the literature at this ionic strength. In Critical Stability Constants (Vol. 4, 1976), Smith and Martell reported four constants, while the NIST issue version 5.0 gives three constants. Table I summarizes some stability constants values of Cd^I chloro complexes. It is obvious that the values obtained by pseudopolarographic measurements are in the range reported by other sources.

Both examples verified the adequacy of using half-wave potentials of reversible pseudopolarograms for the determination of stability constants of simple labile complexes based on the DeFord-Hume method.

Systems with Variable Reversibility

The DeFord-Hume method was originally developed for reversible electrochemical systems. It has been shown that this method can be successfully applied to non-reversible systems in which the reversibility does not change during metal titration with the ligand.[24–27] However, there are systems in which the reversibility of the electrochemical reaction changes with the electrolyte composition. Examples of such systems are electrochemical reactions of zinc(II) oxalato complexes[44] and bismuth(III) chloro complexes.[45–47]

As demonstrated in our previous paper,[32] there is a part at the foot of the normalized (pseudo)polarogram (presented as a log I *vs.* E_{dep} dependence) with a reversible slope. The extension of this part depends on the reversibility. For reversible (pseudo)polarograms it is lengthened over a large part of the total curve (about 20 %), while for quasireversible and irreversible systems the upper limit reaches lower percentages. For quasireversible and irreversible systems, the upper limit depends on the deposition time, electrode size and the diffusion layer thickness.

Two similar methodologies for determination of "critical" potential can be used to calculate stability constants: (i) graphical – evaluation of potentials at a fixed percentage of normalized (pseudo)polarograms in the part with the reversible slope, and (ii) numerical/graphical – comparison of simulated and experimental (pseudo)polarograms for which a "formal" potential will be estimated. The latter method is more adequate since pseudopolarograms are compared in the whole potential range (but also mainly based on the part where curves have reversible slopes), whereas in the former method, only a narrow part of the experimental curve is available for determination of an acceptable potential. In both approaches, the "expert eye" has the crucial role. The baseline subtraction and normalization is the essential step in obtaining accurate "critical" potentials[12,13] (especially for nonreversible pseudopolarograms), as well.

Zinc(II) Oxalato Complexes

Reversibility of the electrochemical reaction of Zn^{II} depends on ionic strength of the supporting electrolyte. In 0.1 mol dm^{-3} $NaClO_4$, the reaction is reversible in the time domain of the polarographic technique, while at higher ionic strengths (≥ 1 mol dm^{-3} $NaClO_4$) the redox reaction approaches quasireversible behavior.[24,25,32,38,48] Complexation parameters of Zn^{II} with various simple ligands were determined by using half-wave potential as the "critical" value for calculations.[24–27] It was shown that the reversibility of the electrochemical reaction of Zn^{II} in 0.16 mol dm^{-3} KNO_3 changes with increasing oxalate concentration.[44] Without added oxalate, the redox reaction is reversible, while with oxalate addition of only 5×10^{-4} mol dm^{-3} a quasireversible character is observed. Moreover, at higher Zn^{II} and oxalate concentrations, formation of sparingly soluble complexes occurs[44] ($\log K_s = 8.1$). By setting the experimental conditions in such a way to ensure that the reversibility of the system was not significantly affected (maximum oxalate concentration was 2.4×10^{-3} mol dm^{-3}), Berbel *et al.* determined stability constants of Zn^{II} oxalato complexes using a classical polarographic technique at a zinc(II) concentration of 9.79×10^{-5} mol dm^{-3}. They calculated stability constants on the basis of the shift of the half-wave potential (or peak potential), which were in good agreement with those reported in the literature.

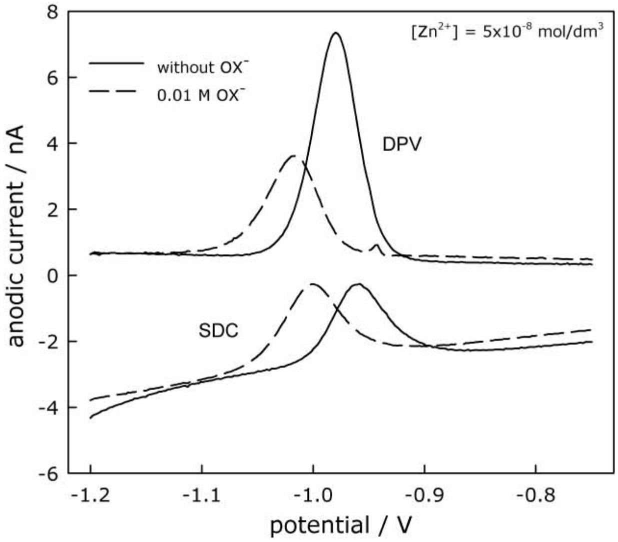

Figure 3. Anodic voltamograms of 5×10^{-8} mol dm^{-3} Zn^{II} recorded by differential pulse and sampled d.c. technique in 0.1 mol dm^{-3} $NaClO_4$ (pH = 4.7) without (solid lines) and with (dashed line) addition of 0.01 mol dm^{-3} of oxalate. Instrument: μ-AUTOLAB; Electrode: Metrohm VA 663; DPASV parameters: $E_i = -1.2$ V, $E_f = -0.75$ V, $E_{\text{sc.inc.}} = 0.002$ V, $A = 0.020$ V, $t_{\text{dep}} = 60$ s, $t_{\text{int}} = 0.1$ s, $t_{\text{mod}} = 0.04$ s; SDCASV parameters: $E_i = -1.2$ V, $E_f = -0.75$ V, $E_{\text{sc.inc.}} = 0.002$ V, $t_{\text{dep}} = 60$ s, $t_{\text{int}} = 0.1$ s.

The same system (zinc(II)–oxalate) is used as a model in the pseudopolarographic determination of stability constants in the system with decreasing reversibility. In our case, measurements were performed in 0.1 mol dm^{-3} $NaClO_4$, (pH = 4.7, 0.024 mol dm^{-3} acetate buffer) at 1×10^{-7} mol dm^{-3} Zn^{II}. Figure 3 shows the anodic stripping voltamograms of 5×10^{-8} mol dm^{-3} Zn^{II} without and with addition of 0.01 mol dm^{-3} oxalate, recorded using differential pulse and sampled d.c. techniques. It is obvious that addition of oxalate into the solution results in a decrease of the DPV peak height, while the peak heights of SDC voltamograms remain unchanged. The following electrochemical reaction mechanism in stripping sequence is supposed: utilizing the differential pulse technique, during the applied potential pulse (at each potential step) a portion of Zn^0 is oxidized; when sufficient concentration of Zn^{II} at the electrode surface is achieved, the sparingly soluble complex is formed; after completing the applied potential pulse (t_{mod}), the subsequent potential is more negative, and the formed sparingly soluble complex is not reduced again to the amalgam. This leads to a successive decrease of zinc in the mercury drop, resulting in a diminished anodic peak. Applying the SDC scanning mode, the formation of such complexes takes place in the vicinity of the mercury drop, as well, but without influencing the signal because of the absence of the reverse po-

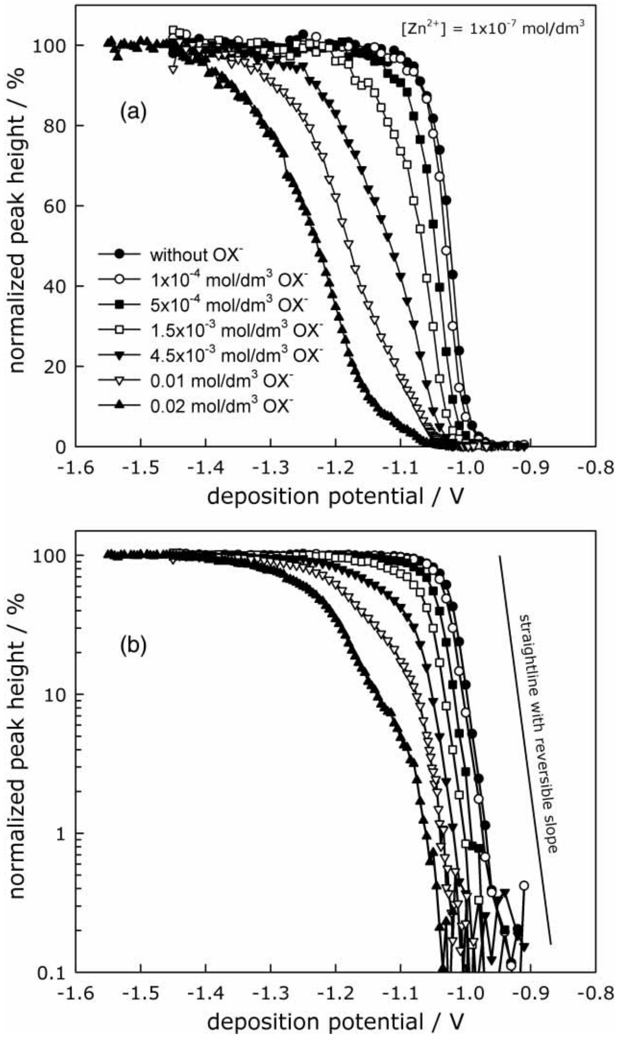

Figure 4. Normalized pseudopolarograms of 1 × 10^{-7} mol dm^{-3} Zn^{II} measured in 0.1 mol dm^{-3} $NaClO_4$ (pH = 4.7) with increasing concentration of oxalate (OX$^-$): (●) without OX$^-$; (○) 1 × 10^{-4} mol dm^{-3} OX$^-$; (■) 5 × 10^{-4} mol dm^{-3} OX$^-$; (□) 1.5 × 10^{-3} mol dm^{-3} OX$^-$; (▼) 4.5 × 10^{-3} mol dm^{-3} OX$^-$; (▽) 0.01 mol/dm^3 OX$^-$; (▲) 0.02 mol dm^{-3} OX$^-$. Electrode: Metrohm VA 663; SDCASV parameters: $E_i = -1.2$ V, $E_f = -0.75$ V, $E_{sc.inc.} = 0.002$ V, $t_{dep} = 60$ s, $t_{int} = 0.1$ s.

tential step. Only a small increase of the half-width of the DPV peak is noticed (<10 %). This is most likely caused by the decrease of the oxidation reaction reversibility. A decrease of the DPV stripping peak is also partly (but not significantly) a result of this process. Hence, the SDC technique is applied for recording voltamograms used for determination of stability constants of Zn^{II} oxalate complexes.

Figure 4 shows normalized pseudopolarograms of Zn^{II} with increasing concentration of the complexing ligand. Pseudopolarograms exhibit a reversible character both without and with oxalate concentration of 1 × 10^{-4} mol dm^{-3}. An additional increase in oxalate concentration to 0.02 mol dm^{-3} results in the reversibility change of the electrochemical reaction to almost irreversible. It is important to note that the limiting current of all pseudopolarograms was not changed by addition of the ligand, implying that the diffusion coefficient was practically the same as for uncomplexed Zn^{II}. Although pseudopolarograms change their shape with decreasing reversibility, there is a visible part at the foot of all curves with a reversible slope (Figure 4b). This part is further exploited for the estimation of the "formal" potential (obtained by comparing experimental and simulated pseudopolarograms), which is then used as the "critical" potential in stability constants calculation. Since the evaluated "formal" potential is not a real formal potential, the kinetic parameters of the electrode reaction, the rate constant (k^o) and the transfer coefficient (α) were not determined. At higher oxalate concentrations (0.01 and 0.02 mol dm^{-3}), a very narrrow range of the reversible part is obtained (< 5 % and < 2 %), but its accurate determination is still possible. The resulting dependence of the "formal" potential shift on the free oxalate concentration is plotted in Figure 5. The "formal" potential of uncomplexed Zn^{II} is corrected by +2 mV due to the complexation with acetate (0.024 mol dm^{-3}). With the first addition of oxalate, the influence of acetate was minimized and further corrections were not done. Free oxalate concentrations at the desired pH and ionic strength were calculated using its protonation constants.[42] For comparison, the shifts of the pseudopolarographic half-wave potential are also marked on the same plot. It is obvious that erroneous stability constants can be obtained by using the shift of the half-wave potential. At higher oxalate concentrations, the ionic strength is slightly increased, but its influence is still in the range of the potential estimation error (about 2 mV). Even with a relatively small number of points, the calculated values of stability constants are in very good agreement with those reported in the literature (Table II).

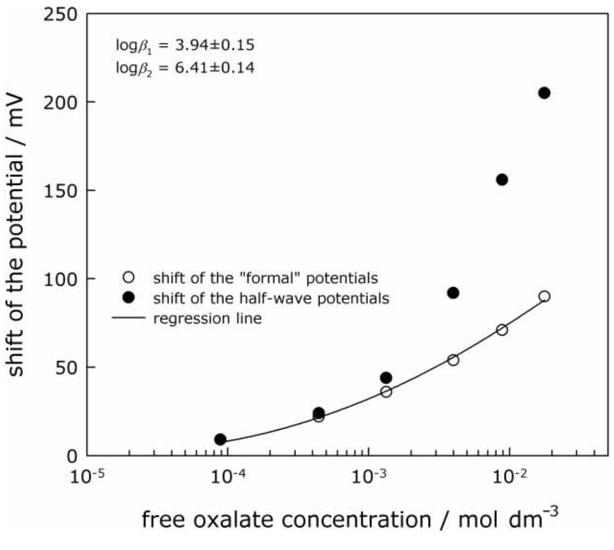

Figure 5. Dependence of the shift of the "formal" potential of 1 × 10^{-7} mol dm^3 Zn^{II} on oxalate concentration.

TABLE II. Stability constants of Zn^{II} oxalato complexes

	This work	Lit. 1[44]	Lit. 2[42]
$\log \beta_1$	3.94 ± 0.15	3.72 ± 0.03	3.83 ± 0.10
$\log \beta_2$	6.41 ± 0.14	6.45 ± 0.05	6.40 ± 0.10

Bismuth(III) Chloro Complexes

The other system with variable reversibility is the electrochemical reaction of Bi^{III} in a perchlorate medium. In 1 $mol\,dm^{-3}$ $HClO_4$, the reduction of Bi^{III} is irreversible,[45–47] while at higher ionic strengths (> 8 $mol\,dm^{-3}$), the reduction becomes reversible. The irreversibility is affected by the slow dehydratation of free Bi^{III} ion, which precedes the charge transfer. Addition of a small concentration of chloride (5×10^{-3} $mol\,dm^{-3}$) or bromide (10^{-4} $mol\,dm^{-3}$) makes the redox reaction reversible. The published rate constant in 1 $mol\,dm^{-3}$ $HClO_4$ is in the range of $3 \times 10^{-5} < k^{o} < 3 \times 10^{-4}$ $cm\,s^{-1}$, and the transfer coefficient is $0.46 < \alpha < 0.68$.[46,48]

Measurements using this system were performed at a constant ionic strength of 1 $mol\,dm^{-3}$ in $(1–x)$ $mol\,dm^{-3}$ $HClO_4 + x$ $mol\,dm^{-3}$ HCl. Concentrations of Bi^{III} ions were 1×10^{-4} and 2×10^{-7} $mol\,dm^{-3}$ in polarographic and pseudopolarographic measurements, respectively. In all measurements, the reference electrode was immersed in a separate jacket filled with supporting electrolyte to exclude leaching of chloride ions into the main solution.

Polarographic Measurements

Figure 6a shows polarograms of 10^{-4} $mol\,dm^{-3}$ Bi^{III} without and with addition of 1×10^{-4}, 5×10^{-4}, 1×10^{-3} and 5×10^{-3} $mol\,dm^{-3}$ of chloride. The polarogram recorded in the absence of chlorides shows an irreversible shape with half-wave potential of 0.015 V. After addition of 10^{-4} $mol\,dm^{-3}$ chloride, the reduction of Bi^{III} became quasireversible, while at 5×10^{-3} $mol\,dm^{-3}$ chloride, the polarogram is fully reversible in the time domain of the used measurement technique. In Figure 6b, normalized polarograms are plotted using the logarithmic ordinate scale. The estimated upper limit of the reversible part of the polarogram without chlorides is 0.3 %, which is below the limit for accurate determination of the »formal« potential. At the chloride concentration of 10^{-4} $mol\,dm^{-3}$, the reversible part reaches 0.6 % of the total current, while at the concentration of 5×10^{-4} $mol\,dm^{-3}$ the curve is reversible below 10 %. Thus, the starting value of the »formal« potential is the same as for the polarogram with the addition of 1×10^{-4} $mol\,dm^{-3}$ of chlorides. The calculated shift of the »formal« potential at 1×10^{-4} $mol\,dm^{-3}$ of chlorides is 0.2 mV. This is in the range of experimental error, and it is assumed that this approximation does not generate a significant error in stability constants calculation. For the calculation of stability constants, »formal« potentials, determined by comparison of the experimental and simulated curves, are used. The dependence of the shift of the »formal« potential on chloride concentrations is shown in Figure 7. For comparison, the points representing the half-wave potentials are plotted on the same graph. The »formal« potential shifts are expressed in relation to the potential obtained in the absence of chlorides. Experimental points are fitted to the model with three, four and five complexes. The fitting using a model with three complex species gave a negative second constant, and the model was *a priori* discarded. Statistical tests on models with four and five complex species supported the formation of four species (Table III).

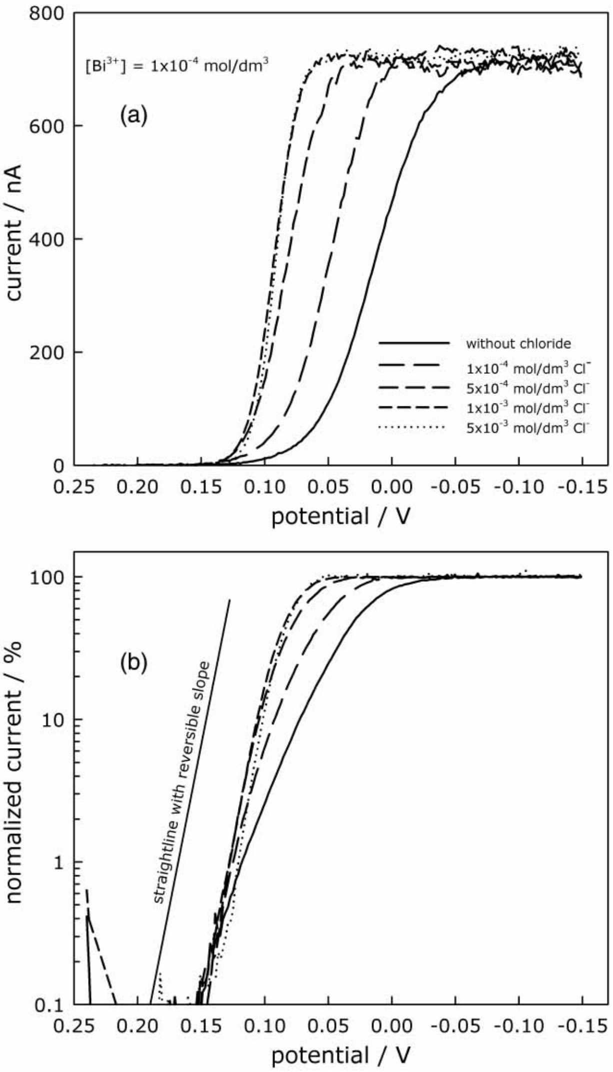

Figure 6. Original (a) and normalized (b) polarograms of 1×10^{-4} $mol\,dm^{-3}$ Bi^{III} measured at constant ionic strength of 1 $mol\,dm^{-3}$ [$(1–x)$ $mol\,dm^{-3}$ $HClO_4 + x$ $mol\,dm^{-3}$ HCl], without and with four increasing concentrations of chloride. Instrument: μ-AUTOLAB; Electrode: modified PAR 303A, small drop size. Sampled d.c. parameters: $E_{sc.inc.} = 0.002$ V, $t_{drop} = 0.5$ s.

TABLE III. Stability constants of Bi^{III} chloro complexes at 1 mol dm^3 ionic strength

	Polarography[(a)]	Pseudopolarography[(a)]	Literature[42]
$\log\beta_1$	2.44 ± 0.07	2.45 ± 0.07	2.4 ± 0.2
$\log\beta_2$	3.61 ± 0.29	3.87 ± 0.20	4.0 ± 0.3
$\log\beta_3$	4.71 ± 0.29	4.64 ± 0.48	5.2 ± 0.3
$\log\beta_4$	5.95 ± 0.04	6.13 ± 0.04	6.4 ± 0.5

(a) Concentration of Bi^{III} ions: 1×10^{-4} mol dm^{-3} in polarographic and 2×10^{-7} mol dm^{-3} in pseudopolarographic measurements.

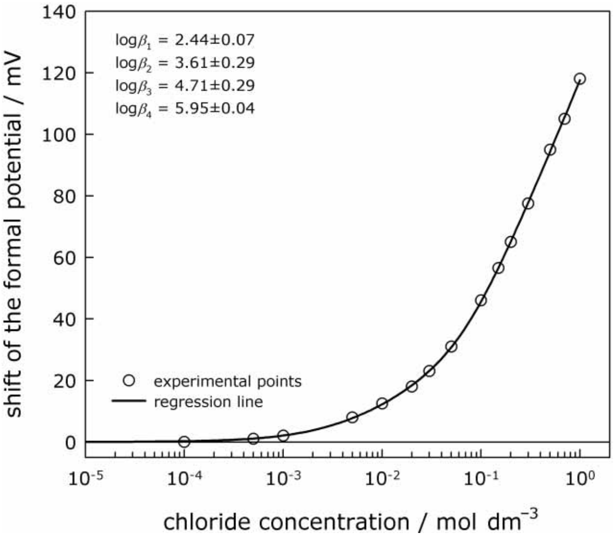

Figure 7. Dependence of the shift of the "formal" potential of 1×10^{-4} mol dm^{-3} Bi^{III} on chloride concentration.

Pseudopolarographic Measurements

Pseudopolarographic measurements were performed in the same way as polarographic measurements, but at a three orders of magnitude lower concentration of bismuth (2×10^{-7} mol dm^{-3}). All pseudopolarograms are presented in Figure 8a. It is obvious that the limiting current increases already with the first addition (1×10^{-4} mol dm^{-3}) and remains constant above the concentration of 5×10^{-3} mol dm^{-3} of chlorides. As shown in Figure 6a, the limiting current is the same for irreversible and reversible polarograms, indicating that the diffusion coefficient does not change with the addition of chlorides. We assume that this increase of the limiting current of pseudopolarograms (Figure 8a) is caused by an increased rate of Bi^0 oxidation, and it is a consequence of the voltammetric technique used for the oxidation (stripping). As the scanning technique was differential pulse voltammetry, an increase of the signal with increased reversibility was expected, which is due to the differential nature of the current sampling during the scanning steps. In Figure 9, voltamograms recorded using differential pulse (a) and sampled d.c. voltammetry (b) are shown for the range of increasing chloride concentrations. Addition of chloride significantly enhances the DPV peak height and shifts the peak potential to more negative values. DPV peak height at a concentration of 5×10^{-3} mol dm^{-3} of chlorides is about five times greater than in the absence of chlorides in the solution, whereas the peak height obtained with the sampled d.c. technique is enhanced by only 60 %. It has been reported in literature that anion induced adsorption occurs at chloride concentrations at which $[BiCl_3]$ and $[BiCl_4]^-$ species are predominant. This can lead to enhancement of the peak height. However, at chloride concentrations below 5×10^{-3} mol dm^{-3}, the concentration of these two species is insufficient to induce an adsorption process. Therefore, the increase of the peak height in this range of chloride concentrations is attributed only to the re-

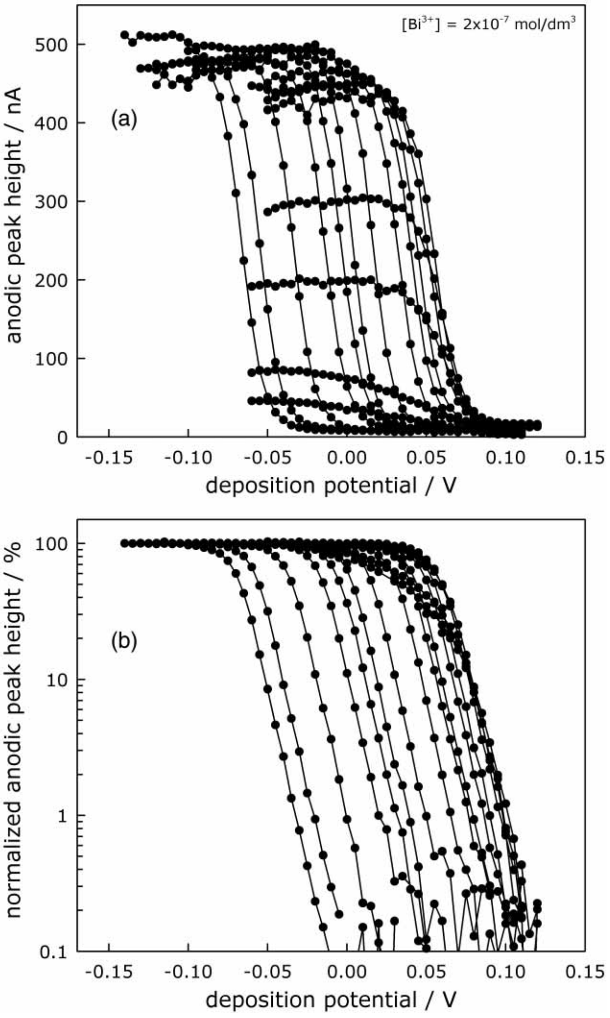

Figure 8. Original (a) and normalized (b) pseudopolarograms of 2×10^{-7} mol dm^{-3} Bi^{III} measured at constant ionic strength of 1 mol dm^{-3} [$(1-x)$ mol dm^{-3} $HClO_4$ + x mol dm^{-3} HCl] with increasing concentration of chloride from 0 to 1 mol dm^{-3}. Instrument: µ-AUTOLAB; Electrode: modified PAR 303A, middle drop size. DPASV parameters: $E_i = -0.05$ to -0.15 V, $E_f = 0.25$ to 0.04 V, $E_{sc.inc.} = 0.002$ V, $A = 0.025$ V, $t_{dep} = 120$ s, $t_{int} = 0.2$ s, $t_{mod} = 0.05$ s.

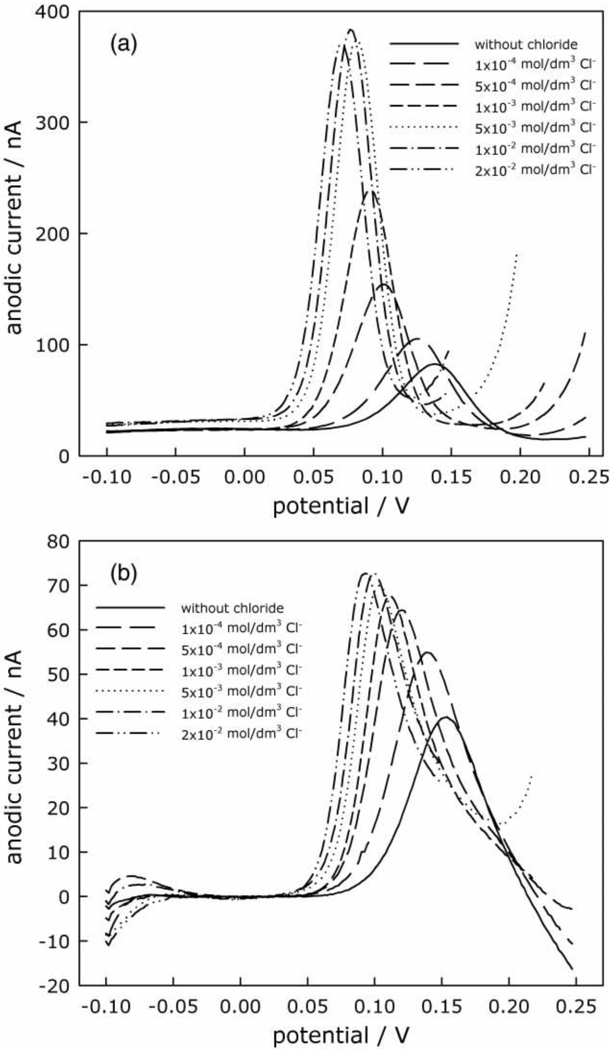

Figure 9. Anodic voltamograms of 2×10^{-7} mol dm^{-3} Bi^{III} recorded by differential pulse (a) and sampled d.c. technique (b) at constant ionic strength of 1 mol dm^{-3} [(1–x) mol dm^{-3} $HClO_4$ + x mol dm^{-3} HCl] with increasing chloride concentration from 0 to 2×10^{-2} mol dm^{-3}. Instrument: μ-AUTOLAB, Electrode: modified PAR 303A, middle drop size. DPASV parameters: E_i = –0.1 V, E_f = 0.25 to 0.15 V, $E_{sc.inc.}$ = 0.002 V, A = 0.025 V, t_{dep} = 120 s, t_{int} = 0.2 s, t_{mod} = 0.05 s; SDCASV parameters: E_i = –0.1 V, E_f = 0.25 to 0.15 V, $E_{sc.inc.}$ = 0.002 V, t_{dep} = 120 s, t_{int} = 0.2 s.

versibility change of the electrochemical reaction in anodic scan. Accordingly, it was assumed that the impact on the determination of stability constants was negligible, and no correction based on the change of the limiting current (associated with the change of the diffusion coefficients) was applied.

Figure 8b shows normalized pseudopolarograms of bismuth (log I vs. E_{dep}) obtained in titration with chlorides. Similarly to polarographic curves, all pseudopolarograms show a reversible part at the foot of the curve (< 1 %). This reversible part was used to manually fit experimental and simulated pseudopolarograms to estimate the "formal" potential and to investigate the dependence of its shift on chloride concentration. Determination of stability constants was performed in the same way as with data obtained by polarographic measurements. The obtained values agree well with those calculated from polarographic measurements, and also with those reported in the literature (Table III).

CONCLUSION

It was found that the stability constants of labile metal complexes (based on the DeFord-Hume method) can be successfully determined using the "critical" potential of pseudopolarographic curves. For simple labile complexes and for reversible behavior, it is not important which part of the total curve will be examined to evaluate such "critical" potential (half-wave, "formal", *e.g.,* potential at 20 % of the entire curve). However, complications emerge when the reversibility of the electrochemical reaction changes with addition of a complexing ligand. In such systems, the half-wave potential cannot be used, and the "critical" potential must be evaluated using the reversible part of the pseudopolarographic curve. This part is located at the foot of the curve, and its range depends on both the reversibility and experimental conditions. It was illustrated that for all four investigated systems, the obtained stability constants were in very good agreement with the literature values.

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SAŽETAK

Pseudopolarografija metala u tragovima. III dio. Određivanje konstanta stabilnosti labilnih metalnih kompleksa

Dario Omanović

Istražene su mogućnosti pseudopolarografske metode u određivanju konstanta stabilnosti labilnih metalnih kompleksa u niskim koncentracijama. Prikazano je kako se metodologija temeljena na DeFord-Humeovu načelu može uspješno primijeniti na podatke dobivene iz pseudopolarograma. Za reverzibilne elektrokemijske sustave, kao što su talij(I)–klorid i kadmij(II)–klorid, za izračun konstanta stabilnosti može se koristiti poluvalni potencijal pseudopolarograma ili odgovarajući "kritični" potencijal. Kao "kritični" potencijal može poslužiti "formalni" potencijal koji se dobiva usporedbom simuliranih i eksperimentalnih (pseudo)polarograma ili potencijal koji se odabire iz područja gdje sve krivulje imaju reverzibilni nagib. Kod sustava s promjenljivom reverzibilnosti elektrokemijske reakcije (cink(II)–oksalat i bizmut(III)–klorid) na pomak poluvalnog potencijala utječe kompleksiranje, ali i promjena reverzibilnosti elektrokemijske reakcije. Poradi toga se za računanje konstanta stabilnosti koristi isključivo "kritični" potencijal. Sve konstante stabilnosti izračunate u ovom radu vrlo se dobro slažu s već publiciranim vrijednostima. Prednost pseudopolarografskoga pristupa je u izbjegavanju različitih smetnja (poput precipitacije, adsorpcije, suviška liganda, itd.) koje mogu utjecati na određivanje konstanta stabilnosti kod visokih koncentracija metala.