

Full-wave analysis of stripping chronopotentiograms at scanned deposition potential (SSCP) as a tool for heavy metal speciation: theoretical development and application to Cd(II)-phthalate and Cd(II)-iodide systems.

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Abstract

A new mathematical treatment has been developed and implemented in an EXCEL spreadsheet in order to determine average equilibrium functions from the full set of data measured by scanning stripping chronopotentiometry (SSCP) in solutions containing different proportions of heavy metal ions and small-sized ligands. It has been applied to the experimental systems Cd(II)-phthalate and Cd(II)-iodide as models of complexation in the absence and in the presence of electrodic adsorption, respectively. The good agreement between the complexation parameters determined in this way, those predicted from literature data and those obtained using a cadmium ion selective electrode (ISE) confirms the validity of the proposed methodology and encourages its further refining for the analysis of macromolecular and heterogeneous systems.

Introduction

It has been recognised that stripping techniques are very effective in the analysis of heavy metal ions in environmental and biological samples [1-4] due to their excellent detection limits, which allows the study at the low concentrations existing in natural media. Stripping techniques applied to heavy metal ions combine a deposition step of metal reduction or adsorption with a stripping step where the accumulated metal is totally or partially dissolved from the electrode back into the solution or, in the case of adsorptive modalities, suffers an oxidation or reduction process from the adsorbed layer.

Stripping chronopotentiometry (SCP), also termed potentiometric stripping analysis (PSA) has been proposed by Jagner and Graneli [5,6] as an alternative to more conventional stripping techniques like anodic stripping voltammetry (ASV). In recent works [7-9] it has been demonstrated that SCP minimizes the problems caused by the adsorption of species onto the mercury electrode.

Constant-current SCP involves a deposition step where the metal is accumulated by reduction into the electrode and a stripping step where it is reoxidised by imposing a constant oxidising current. Then, SCP measures the evolution of the potential as a function of time and uses the transition time (τ), that between successive potential jumps, as the main analytical parameter.

There are some theoretical considerations and experimental experience on the use of constant-current SCP with hanging mercury drop electrode (HMDE) [7,10] and with rotating disk mercury film electrode (MFE-RDE) [11] for heavy metal speciation. In these works the effect of SCP oxidative current on the stripping regime in both HMDE

and MFE-RDE electrodes was studied. In the case of HMDE [10,11] the presence of three characteristic regions was confirmed: high currents ensure semi-infinite linear diffusion, low currents produce total depletion and very low currents suffer from interference of dissolved oxygen. In MFE-RDE [11], the total depletion regime predominates in a wide range of oxidation currents. Despite the potential advantages of SCP, the potential-time characteristic of SCP is quite complicated and in some cases this renders the interpretation of metal complexation by SCP measurements rather difficult.

Stripping chronopotentiometry at scanned deposition potential (SSCP) has been introduced recently [12,13] as an alternative to scanned stripping voltammetry (SSV), a technique previously known as pseudopolarography, which consists in performing ASV measurements at different deposition potentials [14,15]. In the scanning modality, SSCP curves are constructed by plotting τ as a function of the deposition potential (E_d), which produces sigmoidal waves. It has been shown that, as it happens with ASV pseudopolarograms [14], the evolution of half-wave potentials of SSCP signals in the presence of complexing agents can be explained in terms of the classical DeFord-Hume method [16]. But if SSCP measurements are performed under depletive conditions (oxidation of all deposited metal), the results are expected to be much less affected by electrodic adsorption [7,8].

The usual way of investigating metal complexation by ASV or SCP is by means of titrations where the ligand is added to the metal or vice-versa. Then, an electrochemical measurement is carried out after every new addition. In the case of SSCP this can be done by fitting the evolution of the limiting current and half-wave potential with the

added concentration to the DeFord-Hume or more sophisticated models. However, this method does not allow to consider a great number of metal-to-ligand ratios due to the large amount of time required to record a full SSCP wave (composed of 20-40 single SCP measurements at different E_d).

An alternative strategy would consist of the more comprehensive analysis of one single full SSCP wave, which effectively includes information at a wide range of metal-to-ligand ratios. This was considered in scanned stripping voltammetry and allowed the fitting of differential equilibrium functions (DEF) to explain the heterogeneous behaviour of humic acids [15]. The main goal of the present work is to investigate the possibility of a full-wave SSCP analysis of relatively simple systems (Cd(II)-phthalate and Cd(II)-iodide as models of small-sized labile complexes in the presence and in the absence of electrodic adsorption, respectively) as a first step to the application to more complicated systems including macromolecular and heterogeneous complexes.

1. Mathematical model

1.1 Assumptions

Let us assume that

i) The process of building up a M^0 concentration inside the drop is much slower than the diffusion of the metal ion M from the solution to the electrode surface [12,17,18]. Thus, for the diffusion of M and ML , quasi-steady-state conditions apply all along the deposition period, bulk concentration values being maintained at a fixed distance $x = \delta$ (i.e. we assume planar finite diffusion). According to this assumption, the concentrations of M and ML at the electrode surface change with time, but

concentration profiles in solution adapt instantaneously to steady state conditions compatible with the corresponding (time dependent) boundary concentrations.

ii) Inside the electrode, there is a flat concentration profile of the reduced metal (due to its small volume and the fast diffusion/homogeneization, see [12,17,18]) with increasing value along the deposition step.

iii) the system $M + L \rightleftharpoons ML$ is labile. This condition practically means that there is equilibrium between the metal and the complex concentrations at any relevant position in time and space, so that

$$K_c = \frac{c_{ML}(x,t)}{c_M(x,t)c_L(x,t)} \quad (1)$$

where K_c is the so-called average equilibrium function [19,20]. For simplicity and adapted to the particular experimental systems studied, we develop here the particular case of excess of ligand and sequential complexation of one metal with various ligands. In this context, c_{ML} indicates the total concentration of complexes having one metal and any number of ligand molecules.

iv) the reduction/reoxidation process is reversible

$$c_{M^0}(0,t) = \exp\left(-\frac{nF}{RT}(E - E^0)\right) c_M(0,t) \quad (2)$$

where n is the number of exchanged electrons, F is the Faraday constant, T is the temperature, E is the potential, E^0 is the standard potential of the redox system, $c_{M^0}(0,t)$ is the concentration of reduced metal inside the mercury drop and $c_M(0,t)$ is the concentration of metal ion at the electrode surface in the solution.

v) All the complexes share a common diffusion coefficient

We assume here that D_{ML} is the common diffusion coefficient to all the complexes. We call ε to its proportion to the free metal diffusion coefficient D_M

$$\varepsilon \equiv \frac{D_{ML}}{D_M} \quad (3)$$

1.2 Computing the bulk concentrations from the limiting stripping time (τ^*)

In the total depletion regime, the metal accumulated in the deposition step is completely reoxidized in a (measured) time τ by imposing a constant stripping current I_s . Thus, the total stripping charge, $I_s \tau$, can be related to the integral of the metal flux crossing the electrode surface during the deposition step. In diffusion limited conditions, labile complexation (i.e. $c_M(0,t) = c_{ML}(0,t) = 0$), assuming steady state in planar geometry and a common diffusion coefficient for all complexes, the metal flux is constant and

given by $D_M \left(\frac{c_M^* + \varepsilon c_{ML}^*}{\delta} \right)$ so that a simple metal mass balance yields:

$$I_s \tau^* = nFAD_M \left(\frac{c_M^* + \varepsilon c_{ML}^*}{\delta} \right) t_d = I_d^* t_d \quad (4)$$

where I_d^* is the deposition current under diffusion limited conditions, τ^* is the corresponding stripping time, t_d is the deposition time and A is the area of the electrode.

Likewise, when only metal is present in the system

$$I_s \tau_M^* = nFAD_M \left(\frac{c_{T,M}^*}{\delta} \right) t_d \quad (5)$$

where τ_M^* indicates the stripping time in the system with the same amount of total metal but no ligand and under diffusion limited conditions.

Dividing (4) by (5) we have

$$c_M^* + \varepsilon c_{ML}^* = c_{T,M}^* \frac{\tau^*}{\tau_M^*} \quad (6)$$

which together with

$$c_M^* + c_{ML}^* = c_{T,M}^* \quad (7)$$

allows the determination of c_M^* and c_{ML}^* from the limiting stripping times of the SSCP waves (i.e. τ^* with and without ligand), provided the value of D_{ML} is known.

In fact, one could relax assumption v) in 1.1 and consider a specific diffusion coefficient for each complex giving rise to dimensionless ratios ε_j . Then, eqn. (6) becomes

$$c_M^* + \sum_{j=1}^n \varepsilon_j c_{ML_j}^* = c_{T,M}^* \frac{\tau^*}{\tau_M^*} \quad (8)$$

This allows to interpret the common ε used in this work as a weighted average of the individual dimensionless diffusion coefficients, because, due to lability, even when we are not working with bulk concentrations

$$\varepsilon = \frac{\sum_{j=1}^n \varepsilon_j c_{ML_j}^*}{c_{ML}^*} = \frac{\sum_{j=1}^n \varepsilon_j c_{ML_j}^*}{\sum_{j=1}^n c_{ML_j}^*} = \frac{\sum_{j=1}^n \varepsilon_j \beta_j (c_L^*)^j}{\sum_{j=1}^n \beta_j (c_L^*)^j} \quad (9)$$

where β_j stands for the cumulative association constant giving rise to ML_j . For each SSCP series at a fixed ligand concentration (in excess), ε is a constant. The differences between ε of different series are considered negligible when compared with the inaccuracies associated to the stability constant we are retrieving, so -in this preliminary work- we take a unique ε for all the complexes of a system.

1.3 Computing the concentrations at the electrode surface from the wave

1.3.1 Computing $c_M(0, t_d)$

The total metal accumulated in the deposition step, $I_s \tau$, can be related to the amount of reduced metal accumulated in the electrode, $nFVc_{M^0}$ (where V is the volume of the mercury electrode), and due to the reversibility of the system via eqn (2), c_{M^0} can be related to $c_M(0, t_d)$:

$$I_s \tau = nFVc_{M^0} = nFV \exp\left(-\frac{nF}{RT}(E_d - E^0)\right) c_M(0, t_d) \quad (10)$$

where E_d stands for the deposition potential applied. Thus, for each couple $[E_d, \tau]$, equation (10) allows the calculation of $c_M(0, t_d)$. In order to minimize drift effects of the reference electrode, equation (10) can be written in terms of $E_{d,1/2,M}$, the half-wave potential of the SSCP wave for the system that contains only metal.

The SSCP wave for the system with only metal takes the form [12]:

$$\tau = \tau_{d,M} \frac{I_d^*}{I_s} \left(1 - \exp\left(-\frac{t_d}{\tau_{d,M}}\right) \right) \quad (11)$$

where

$$\tau_{d,M} = \frac{\delta V}{AD_M} \exp\left(-\frac{nF}{RT}(E_d - E^0)\right) \quad (12)$$

I_s and I_d^* are respectively, the stripping and the deposition current in diffusion limited conditions.

Defining a dimensionless time $u = \frac{t_d}{\tau_{d,M}}$, the expression for the SSCP wave (11)

combined with eq (4) takes the form:

$$\frac{\tau}{\tau^*} = \frac{\tau_{d,M}}{t_d} \left(1 - \exp\left(-\frac{t_d}{\tau_{d,M}}\right) \right) = \frac{(1 - \exp(-u))}{u} \quad (13)$$

The condition of the half wave potential is $\frac{\tau}{\tau^*} = \frac{1}{2}$. Applied to (13) gives $u_{1/2} = 1.5936$

[9]. Using the definition of $\tau_{d,M}$, eqn. (12),

$$u_{1/2} = \frac{t_d}{\tau_{d,1/2,M}} = \frac{t_d AD_M}{\delta V} \exp\left(\frac{nF}{RT}(E_{d,1/2,M} - E^0)\right) \quad (14)$$

Isolating $c_M(0, t_d)$ in (10), replacing I_s from eqn (4) for a case with just metal, and using (14), we obtain

$$c_M(0, t_d) = u_{1/2} c_{T,M}^* \frac{\tau}{\tau_M^*} \exp\left(\frac{nF}{RT}(E_d - E_{d,1/2,M})\right) \quad (15)$$

where τ_M^* is the limiting stripping time of the system with only metal present for $E_d \ll E^0$.

1.3.2 Computing $c_{ML}(0, t_d)$

For fully labile systems, the boundary condition at $x=0$ can be written as

$$AD_M \left[\left(\frac{dc_M(x,t)}{dx} \right)_{x=0} + \varepsilon \left(\frac{dc_{ML}(x,t)}{dx} \right)_{x=0} \right] = V \left(\frac{dc_{M^0}(0,t)}{dt} \right) \quad (16)$$

As $c_M(x,t) + \varepsilon c_{ML}(x,t)$ has a linear concentration profile under steady state conditions,

using (2) in the right hand side of (16), we have

$$AD_M \frac{c_M^* + \varepsilon c_{ML}^* - c_M(0,t) - \varepsilon c_{ML}(0,t)}{\delta} = V \exp\left(\frac{-nF}{RT}(E_d - E^0)\right) \left(\frac{dc_M(0,t)}{dt}\right) \quad (17)$$

which, using (14) becomes

$$\frac{t_d}{u_{1/2}} \exp\left(-\frac{nF}{RT}(E_d - E_{d,1/2,M})\right) \left(\frac{dc_M(0,t)}{dt}\right) = c_M^* + \varepsilon c_{ML}^* - c_M(0,t) - \varepsilon c_{ML}(0,t) \quad (18)$$

Eqn. (18) is an algebraic equation for $c_{ML}(0,t_d)$ whose solution requires the knowledge of $\left(\frac{dc_M(0,t)}{dt}\right)$. However, in SSCP we only determine τ at the end of a fixed deposition

time t_d . The key point to solve this problem comes from the use of a new dimensionless variable defined as

$$\xi = \frac{u_{1/2} t}{t_d} \exp\left(\frac{nF}{RT}(E_d - E_{d,1/2,M})\right) \quad (19)$$

Using this variable, eqn. (18) rewrites

$$\frac{dc_M(0,\xi)}{d\xi} = c_M^* + \varepsilon c_{ML}^* - c_M(0,\xi) - \varepsilon c_{ML}(0,\xi) \quad (20)$$

With the change of variables given by (19), time and potential influences are embedded in the new variable, ξ . As we are using different deposition potentials along the wave, we can numerically obtain the derivative of $c_M(0,\xi)$ with respect to ξ . With this derivative at hand, (20) allows the calculation of $c_{ML}(0,\xi)$ once $c_M^* + \varepsilon c_{ML}^*$ is known (for instance via eqn. (6)).

1.3.3 Computing K_c and checking consistency of results

The knowledge of a set of couples (E_d, τ) can yield $c_M(0,t_d)$ and $c_{ML}(0,t_d)$ via eqns (15) and (20) for the different deposition potentials along an SSCP wave. The

computation of K_c (eqn 1), for each of these deposition potentials is then straightforward. As shown in the Results section, in the case of sequential complexation and excess of ligand, this K_c should remain essentially constant for a given concentration of ligand.

Notice that $c_M(0, t_d)$ and $c_{ML}(0, t_d)$ should tend to c_M^* and c_{ML}^* in the limit of less negative deposition potentials, i. e., at the potentials corresponding to the foot of the SSCP wave which corresponds to the conditions sought by the technique AGNES [18,21]. So, in this region, eqn. (15) reverts essentially to (10) with $c_M(0, t_d) = c_M^*$ and provides another independent way of obtaining c_M^* to that outlined around eqns. (6)-(7), just using a quite apart region of the SSCP wave.

2. Experimental section

2.1 Reagents

All reagents used were Merck analytical grade. Solutions of phthalate were prepared from potassium hydrogenphthalate and partially neutralized with KOH until pH 5.5, KNO_3 0.01 mol L^{-1} was employed as the supporting electrolyte. Iodide solutions were prepared from potassium iodide and standardized according to Volhard method [22], KNO_3 0.1 mol L^{-1} was applied as supporting electrolyte. Cd(II) stock solution of $1 \times 10^{-2} \text{ mol L}^{-1}$ was prepared from $Cd(NO_3)_2 \cdot 4H_2O$ and standardized complexometrically [22]. The diffusion coefficient of the uncomplexed metal ion is $0.72 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [23]. Ethylenediamine obtained from Aldrich (purity higher than 99%) was employed as

complexing ligand for the calibration of cadmium ion selective electrode (Cd-ISE). Ultrapure water (Milli-Q plus 185 system, Millipore) was used in all experiments.

2.2 Apparatus and Electrochemical parameters

Stripping chronopotentiometry at scanned deposition potential (SSCP) measurements were performed in an Autolab System PGSTAT12 (EcoChemie, The Netherlands) attached to a Metrohm 663 VA Stand (Metrohm, Switzerland) and a personal computer with GPES version 4.9 data acquisition software (EcoChemie). The system was also connected to a Metrohm 665 Dosimat for the addition of solutions and to an Orion SA 720 pH-meter for monitoring the pH value during the experiments. Calibration according to the literature [24] and measurements with cadmium ion selective electrode (Metrohm, Switzerland) were carried out with 809 Titrando (Metrohm, Switzerland) and a personal computer with Tiamo version 1.0 software. All the measurements were performed in a glass cell at constant room temperature (25 °C) under a purified nitrogen atmosphere (Air Liquide).

In all cases the reference electrode, to which all potentials are referred, was Ag|AgCl|KCl (3 mol L⁻¹) separated from the measurement solution by a liquid junction containing KNO₃ 0.1 mol L⁻¹ to prevent contamination of the sample by chloride ions. The counter electrode was a glassy carbon electrode. A hanging mercury drop electrode (HMDE) was used as a working electrode producing drops of ca. 0.5 mm² (which allows sphericity effects to be neglected).

In chronopotentiometric measurements deposition potentials between -0.88 and -0.58 V were applied during 90 s and a rest period of 5 s was performed at the same deposition potential between the deposition and the stripping steps. The SCP oxidising current, I_s , was 1×10^{-8} A, which corresponds to conditions approaching complete depletion ($I\tau$ constant) [10]. The transition time was measured as the area under the baseline-

corrected dt / dE plot, which according to previous work [10], minimises the contribution of capacitive currents and other secondary effects. The SSCP waves were constructed from a series of individual measurements of peak areas plotted as a function of the wide range of deposition potentials (E_d) applied.

2.3 Chronopotentiometric titration

Each titration started by placing in the cell a volume of 25 mL of a solution containing Cd(II)-ion and 0.01 mol L⁻¹ of KNO₃ (in the case of the Cd-phthalate) or 0.1 mol L⁻¹ of KNO₃ (in the case of the Cd-iodide). Then, the sample was deaerated with pure nitrogen for 30 min and for each point of the SSCP wave, the potential was held at the value chosen for the E_d for the duration of the deposition time (t_d) with solution stirring, followed by a rest period (without stirring), after which time the I_s was applied. Further, aliquots of phthalate or iodide were added and the respective curves were recorded. All solutions were deaerated and mechanically stirred for 30 s after each scan and for 3 min after each addition.

In order to prevent changes in ionic strength, the solution to be added contained the same concentration of KNO₃ as in the cell.

2.4 Calibration of Cd-ISE

The nominal measurable concentration range of the Cd-ISE was 10⁻¹ to 10⁻⁷ mol L⁻¹ but as shown in Figure 1a, the calibration titration when Cd²⁺ is added to a KNO₃ solution reveals that Nernstian response is deteriorated below pCd ~ 5.

A previous work [24] has proved that the use of ethylenediaminetetraacetic acid (EDTA) or ethylenediamine (*en*) as complexing ligands increases the range in which the Cd-ISE has a Nernstian response.

In this work ethylenediamine (*en*) was selected as complexing ligand and the electrode behaviour was determined by measuring solutions containing different amounts of *en* (0.1 mol L^{-1}) with $1 \times 10^{-3} \text{ mol L}^{-1} \text{ Cd}(\text{NO}_3)_2$ in a range of free Cd from pCd 3 to pCd 10.3. These solutions were prepared the day before the measurement, so that, despite the slow kinetics between Cd^{2+} and *en*, the equilibrium state is reached.

Figure 1b and 1c show the calibration curves obtained for cadmium ISE in *en* solutions at 0.01 mol L^{-1} and 0.1 mol L^{-1} of ionic strength respectively. As shown, when a total cadmium concentration of $1 \times 10^{-3} \text{ mol L}^{-1}$ is used, the Cd-ISE has a Nernstian response in a wide range of free metal ion concentrations; but when the total concentration of the metal (free + complexed) decreases, the Nernstian response is deteriorated. As shown in Figure 2 for $1 \times 10^{-5} \text{ mol L}^{-1}$ of total cadmium concentration, the Cd-ISE has a Nernstian behaviour until pCd ~ 9 , but for a total concentration of $1 \times 10^{-6} \text{ mol L}^{-1}$ the Nernstian response of the Cadmium ISE is deteriorated below pCd ~ 7 .

Thus, taking into account that in the study of our systems the total cadmium concentration is $1 \times 10^{-6} \text{ mol L}^{-1}$, measurements with Cd-ISE only will be possible for concentrations of free cadmium (c_{Cd}^*) higher than $1 \times 10^{-7} \text{ mol L}^{-1}$.

3. Results and discussion

3.1 Study of the Cd^{2+} -phthalate system as a model of small labile complexes without electrodic adsorption

Figure 3 shows the SSCP curves obtained during the depletive chronopotentiometric titration of $10^{-6} \text{ mol L}^{-1} \text{ Cd}(\text{II})$ solution with phthalate (free ligand concentrations 0 , 1.22×10^{-3} , 5.89×10^{-3} and $2.15 \times 10^{-2} \text{ mol L}^{-1}$) at pH 5.5 and ionic strength of 0.01 mol L^{-1}

using a HMDE. The SSCP curves decrease in height and progressively shift towards more negative potentials with the addition of the ligand. This is consistent with the expected formation of electrochemically labile complexes of stoichiometry 1:1 and 1:2 with diffusion coefficients smaller, but still relatively similar to those of free metal ions [7,16].

SSCP-Analyzer is a spreadsheet (available free of charge at <http://web.udl.es/usuaris/q4088428/Publicacions/Publicacions.html>) for the calculation of $c_M(0, t_d)$ via eq. (10), $c_{ML}(0, t_d)$ via (20) and K_c via (1) from SSCP waves. The first step consists in introducing some parameters such as: deposition time (t_d), number of exchanged electrons (n), SSCP half wave potential in the absence of ligand ($E_{d,1/2,M}$), total ligand concentration ($c_{T,L}^*$), total metal concentration ($c_{T,M}^*$), diffusion coefficient of the metal ion (D_M), diffusion coefficient of the complex (D_{ML}), the maximum transition time in the SSCP wave in the presence of ligand (τ^*), the maximum transition time in the SSCP wave in the absence of ligand (τ_M^*) and some other constants. Then, the full wave (i.e. the couple E_d, τ) has to be introduced to the spreadsheet.

As explained in subsection 1.3.3, the free cadmium concentration (c_{Cd}^*) is obtained by SSCP Analyzer via two different ways. One estimated value of c_{Cd}^* comes from the value of $c_M(0, t_d)$ at potentials in the foot of wave (i.e. deposition potentials slightly less positive than its half-wave potential), using eqn. (15), as with these deposition potential, equilibrium conditions can be practically reached, as extensively exploited by the technique AGNES [18,21]. The second value of c_{Cd}^* results from the simultaneous solution of eqns. (6) and (7), based on the deposition step being all the time under

diffusion limited conditions. We have fitted the ε -value so that these two c_{Cd}^* -values, in all the experiments, are optimally close to each other. In the particular case of Cd-Phthalate system the fitted ε -value for the complexes is 0.923.

The values of free phthalate concentration ($[\text{Ph}^{2-}]$) all along this work have been calculated with the total ligand concentration added, ignoring any Cd^{2+} concentration (because we are in ligand excess conditions) and taking into account the protonation of phthalate at pH 5.5 and ionic strength 0.01 mol L^{-1} using MINTEQA2 [25].

Table 1 shows a reasonable agreement between the values of c_{Cd}^* obtained from the two different computations by SSCP Analyzer and from literature data [26,27]. Measurements with Cd-ISE carried out for the two first additions of phthalate, corresponding to a free cadmium concentration higher than $1 \times 10^{-7} \text{ mol L}^{-1}$, have been included and they are also consistent. The agreement with published data is especially remarkable if we take into account the inherent complexity of this determination, corroborated by the discrepancies reported by different sources.

As two successive Cd-Phthalate complexes have been described [28], under excess ligand conditions, K_c given in eqn (1) can be written as:

$$K_c = \frac{c_{\text{ML}}}{c_{\text{M}}c_{\text{L}}^*} = \beta_1 + \beta_2 [\text{Ph}^{2-}] \quad (21)$$

where β_1 and β_2 are the overall stability constants of CdPh and CdPh_2^{2-} complexes respectively. Table 2 contains different values found in the literature [26,27] once corrected to ionic strength 0.01 mol L^{-1} . $[\text{Ph}^{2-}]$ indicates the bulk concentration of free

phthalate (which is constant for any point in solution, at any time and along the SSCP wave for each addition of the titration under the studied conditions).

Table 3 compares the expected values of K_c with those obtained via computation with SSCP Analyzer for the experiments at different phthalate concentrations, showing a reasonable agreement with each other.

Alternatively, we can estimate the cumulative complexation constants from the K_c retrieved by SSCP-Analyzer using eqn (21) with β_1 and β_2 as unknowns and K_c values taken from first column in Table 3. The cumulative stability constants β_1 and β_2 obtained in this way are gathered in the first row of Table 2 and the fitted curve is shown in Figure 4. As it can be seen, despite the large uncertainty of the calculations (3 points to fit a line), the stability constants obtained are relatively close to the literature values and the standard deviations of the fitting are quite small.

3.2 Study of the Cd^{2+} -iodide system as a model of small labile complexes with electrodic adsorption

The Cd(II)-iodide system has been previously studied by different techniques and complexes of stoichiometry ranging from 1:1 to 1:4 have been found depending on the experimental conditions [29]. The iodide has the advantage of not having reactions with protons, but the difficulty of the well-known presence of adsorption phenomena of iodide ions and induced adsorption of Cd on the mercury electrodes [30-33]. So, this system has been selected in order to check whether the impact of adsorption can be a hindrance for the current methodology. Depletive SSCP measurements have been

carried out in this work during the titration of solutions containing 10^{-6} mol L⁻¹ of Cd(II) with iodide at pH 5.5.

Figure 5 shows the SSCP curves obtained using a HMDE. The addition of the ligand produces a shift of the sigmoidal curve to more negative potentials and a slight increase in the curve height, that confirms some previous results [34-36] showing higher diffusion coefficients for the Cd-I complexes as compared to Cd²⁺ alone. The waves are also consistent with the expected electrochemically labile behaviour of the Cd²⁺-iodide complexes. On the other hand, as discussed in the classical literature [38, 39], reactant adsorption can produce distortion of polarographic waves, with the appearance of pre- and post-waves and peaks. Thus, by analogy, adsorption could produce also some kind of distortion (e.g., deformed shape or splitting) in the individual dt/dE SCP peaks whose areas provide the points in SSCP plots, especially at the less negative deposition potentials. However, all individual SCP signals obtained in the presence of iodide (not shown) presented the same regular peak shape as for Cd²⁺ alone and only a slight broadening was detected at increasing concentrations of iodide. Such broadening suggests that adsorption could be present in SCP measurements, but also that its influence on the results should be small (especially considering that the transition times are measured as peak areas and not peak heights).

In such SSCP experiments (carried out at free iodide concentration 0, 1.48×10^{-3} , 1.09×10^{-2} , 2.05×10^{-2} , 7.68×10^{-2} and 1.01×10^{-1} mol L⁻¹), the transition time of each individual SCP measurement and the half wave potential in only metal SSCP wave (iodide concentration 0 mol L⁻¹) were measured.

General parameters of the Cd^{2+} -iodide system, constants and values of transition time obtained for each deposition potential applied were introduced into the SSCP Analyzer, which computed $c_M(0, t_d)$ via eq. (12), $c_{ML}(0, t_d)$ via (22) and K_c via (1).

As done in the case of Cd+Phtalate, we have fitted ε so that the two values of the free cadmium concentration (c_{Cd}^*) provided by SSCP Analyzer converge for each concentration of iodide concentration. The value found was $\varepsilon = 1.36$, which indicates that the mobility of the complexes Cd+I is larger than the mobility of the hydrated Cd-ion, as already described in the literature [34-36]. Table 4 summarizes these c_{Cd}^* values obtained by the analysis of the foot of wave and from the limiting transition time, which are reasonably close to each other and to those obtained by measurements with Cd-ISE and literature data [26].

Table 5 compares the values of K_c , at different iodide concentration, obtained experimentally by SSCP Analyzer computation and the theoretically expected values of K_c calculated according to this equation:

$$K_c = \beta_1 + \beta_2 [\text{I}^-] + \beta_3 [\text{I}^-]^2 + \beta_4 [\text{I}^-]^3 \quad (22)$$

where β_1 , β_2 , β_3 and β_4 are the overall stability constants of CdI^+ , CdI_2 , CdI_3 and CdI_4^{2-} complexes respectively and their values have been taken from the literature [26,37] and adapted to ionic strength 0.1 mol L^{-1} .

Table 5 shows that the values of K_c found by SSCP Analyzer for the five iodide concentrations are quite similar to the values expected. This fact suggests that the

influence of adsorption on the mercury electrode is really minimized by depletive SCP measurements.

Table 6 reports the values of the cumulative stability constants obtained by a least squares fitting of equation (22) to the experimental set of $[\Gamma]$ and K_c values. The corresponding fitted curve is shown in Figure 4.

In the analysis of Table 6, the same uncertainties discussed for the case of phthalate have to be admitted (now, 5 points are used to fit 4 constants). Anyway, these results also exhibit a reasonable agreement of the $\log \beta_n$ estimated from experimental data and values reported in the literature [27, 40].

4. Conclusions

A new numerical data treatment has been derived to fully analyze the deposition potential scanned stripping chronopotentiometry (SSCP) waves, for depletive stripping, at conventional HMDE.

For fully labile systems, it has been shown that the time and potential dependence of the metal concentration at the electrode surface in an SSCP experiment of an electrochemical reversible system reduces to just a combined dependence in terms of a dimensionless variable ξ , (given by eqn (19)). This combined dependence enables the use of a change of variables expression (see eqn (20)) which leads to the direct determination of K_c with a great save of computational work. A simple Excel spreadsheet, the SSCP-Analyzer, includes all the calculations.

The full-wave SSCP analysis has been applied to two relatively simple systems, Cd(II)-phthalate and Cd(II)-iodide, as models of small labile complexes in the presence and in the absence of electrodic adsorption, respectively.

SSCP curves, τ versus E_d , obtained during the depletive chronopotentiometric titration of 10^{-6} mol L⁻¹ Cd(II) solution with phthalate at pH 5.5 and ionic strength of 0.01 mol L⁻¹, lead to the determination of K_c and the overall stability constants of CdPh⁺ and CdPh₂, β_1 and β_2 , in accordance with literature values.

Also a good agreement results in the determination of K_c and the different successive stability constants, β_1 , β_2 , β_3 and β_4 , for the Cd/iodide SSCP curves at the same conditions, but with 0.1 M ionic strength, suggesting that SSCP minimizes electrodic adsorption effects, as already shown in the literature [7-9].

The free metal concentration computed from the full-wave strategy in both systems also coincides with potentiometric measurements carried out with a cadmium ISE.

Further work considering heterogeneous complexants and non-excess ligand conditions could be tackled developing the theoretical framework here expound.

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Symbols and abbreviations

A	electrode surface area
ASV	anodic stripping voltammetry
β	overall stability constant
DEF	differential equilibrium functions
c_L	concentration of ligand
c_M	concentration of metal ion
c_{M^0}	concentration of reduced metal in the mercury drop
c_M^*	concentration of metal ion in the bulk solution
c_{ML}	concentration of complexed metal
c_{ML}^*	concentration of complexed metal in the bulk solution
$c_{T,M}^*$	total metal concentration in the bulk solution
δ	diffusion layer thickness
D	diffusion coefficient
E	potential
E_d	deposition potential
$E_{d,1/2,M}$	half-wave potential of the SSCP wave for a solution containing only metal
ε	ratio of the diffusion coefficients D_{ML}/D_M
E^0	standard potential of the redox system
F	Faraday constant
HMDE	hanging mercury drop electrode
I_d^*	limiting deposition current

I_s	SCP stripping current
ISE	ion selective electrode
K_c	average equilibrium function
L	ligand
M	free metal ion
ML	complexed metal ion
MFE	mercury film electrode
n	number of exchanged electrons
PSA	potentiometric stripping analysis
RDE	rotating disk electrode
SCP	stripping chronopotentiometry
SSCP	stripping chronopotentiometry at scanned deposition potential
SSV	scanned stripping voltammetry
t	time variable
T	Temperature
t_d	deposition time
τ	SCP transition (stripping) time
τ^*	SCP limiting τ value
τ_M^*	SCP limiting τ value for a solution containing only metal
$\tau_{d,M}$	characteristic time constant of the deposition process for a solution containing only metal
V	volume of the mercury electrode
x	spatial variable
ξ	dimensionless variable

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Figure 1

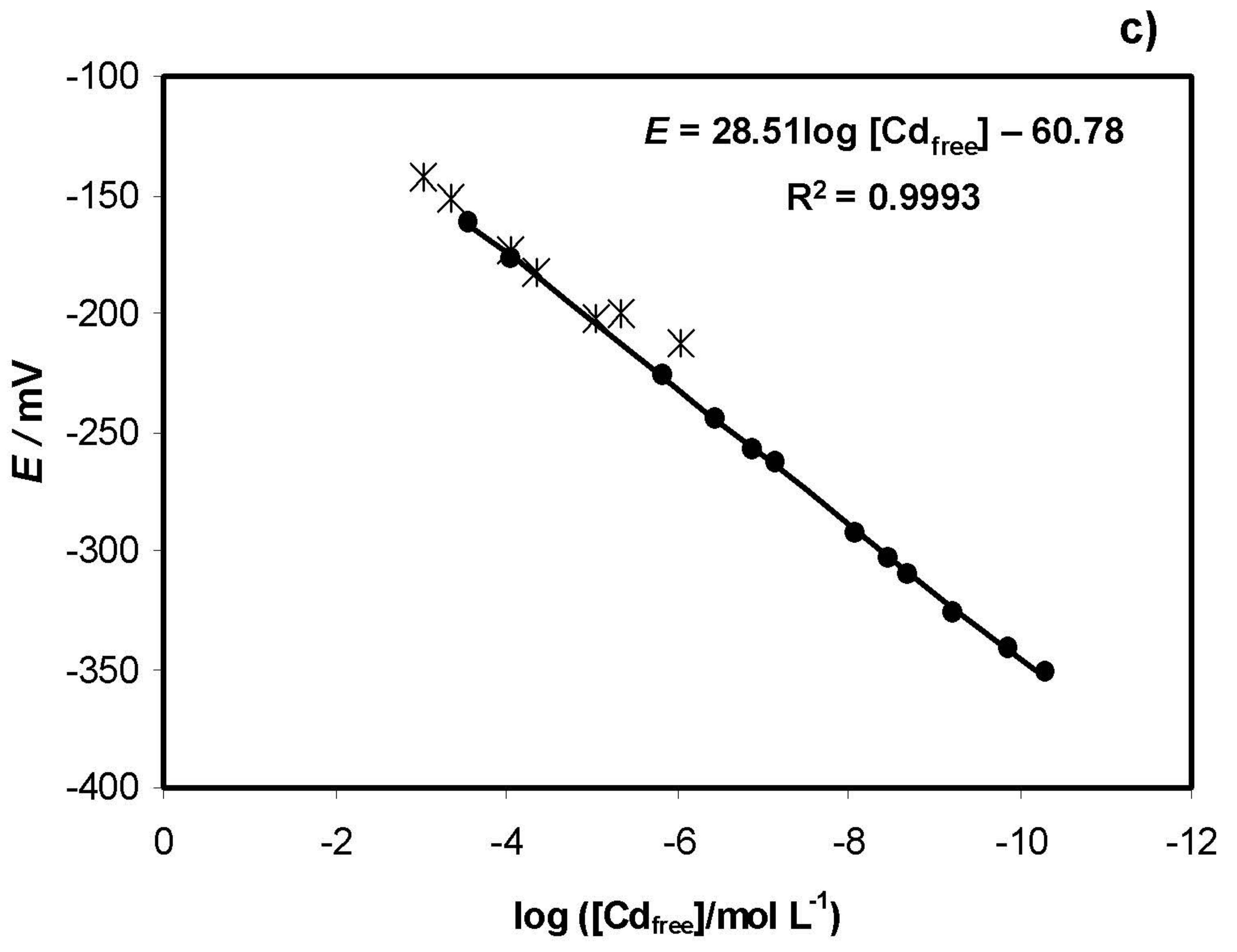
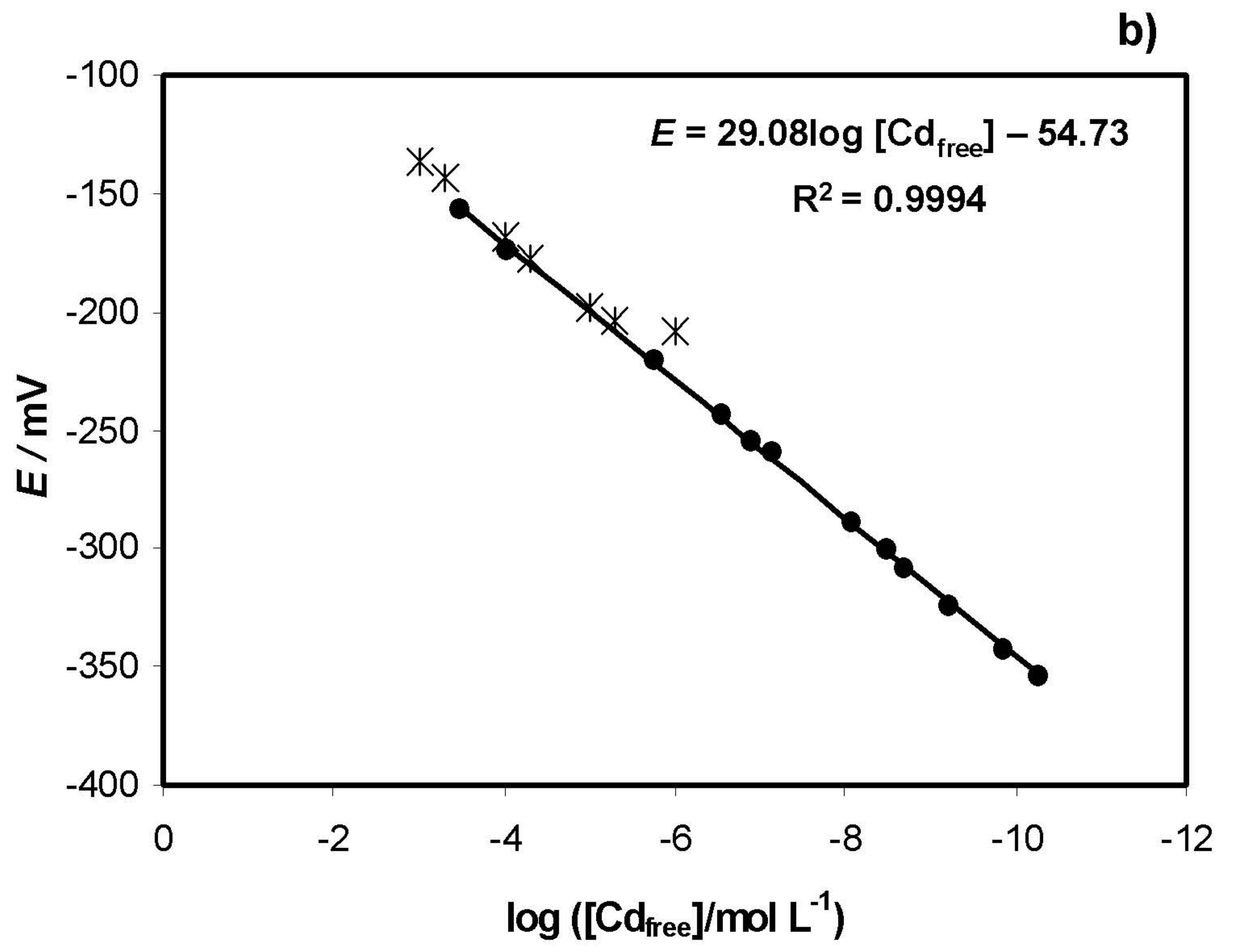
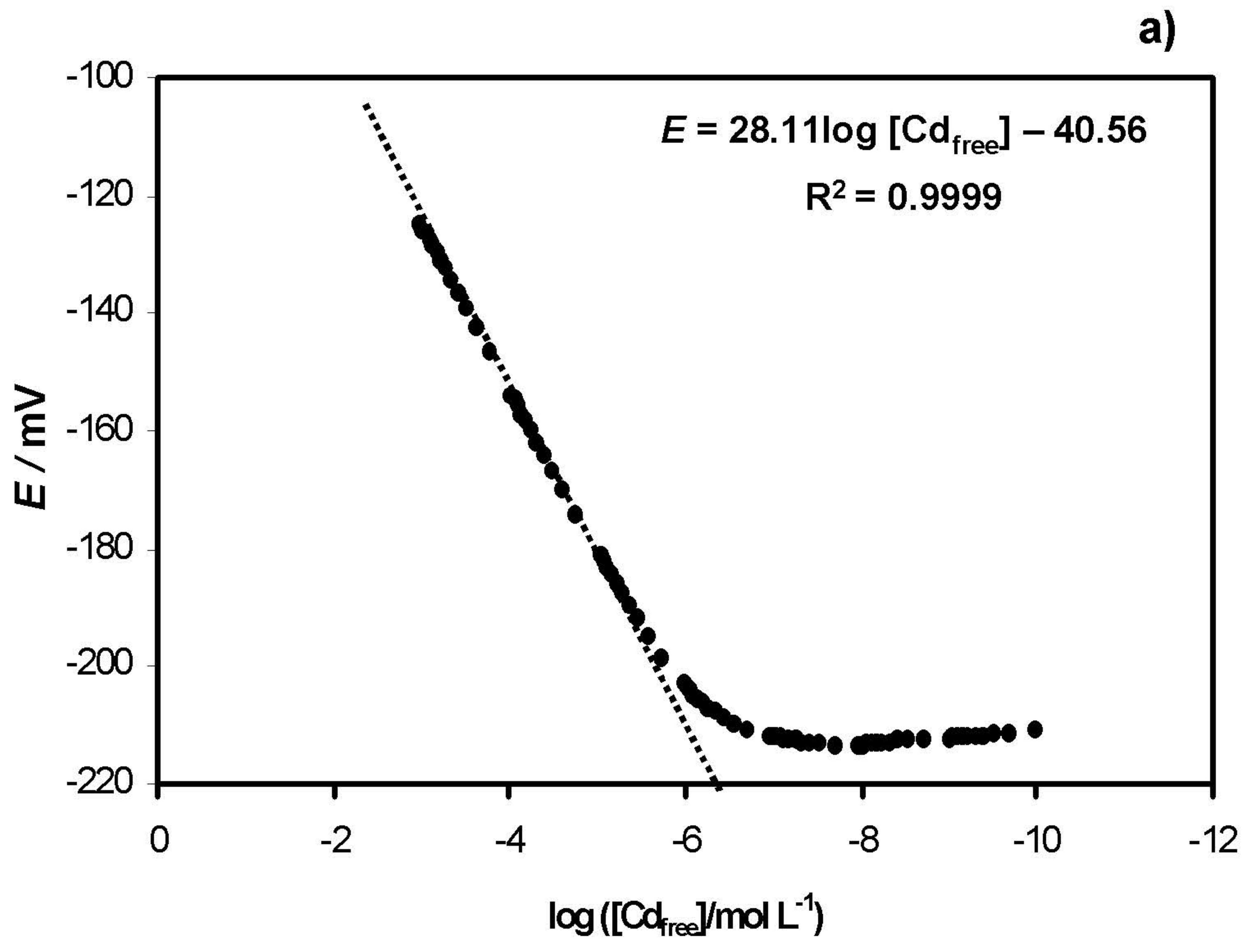


Figure 2

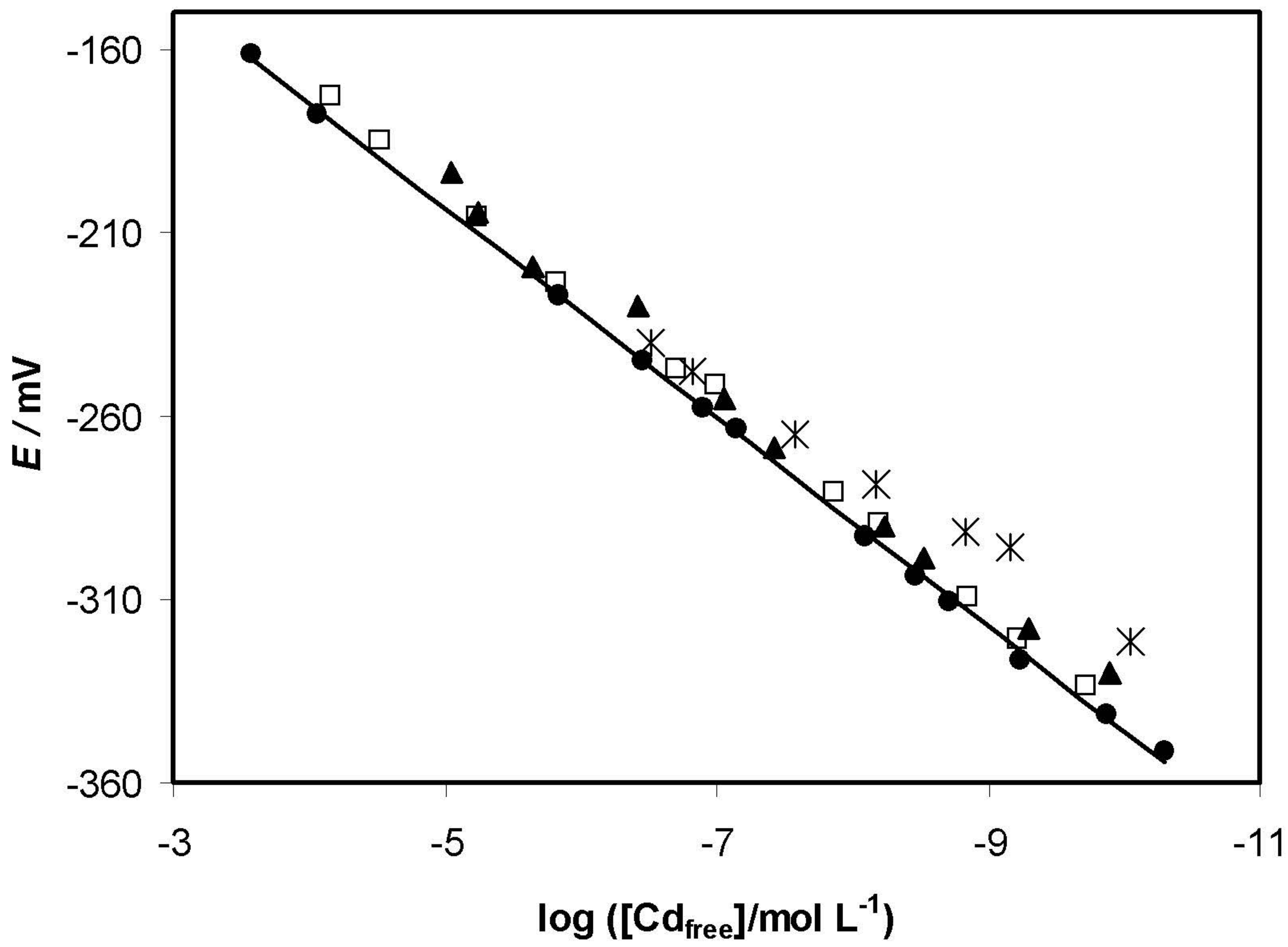


Figure 3

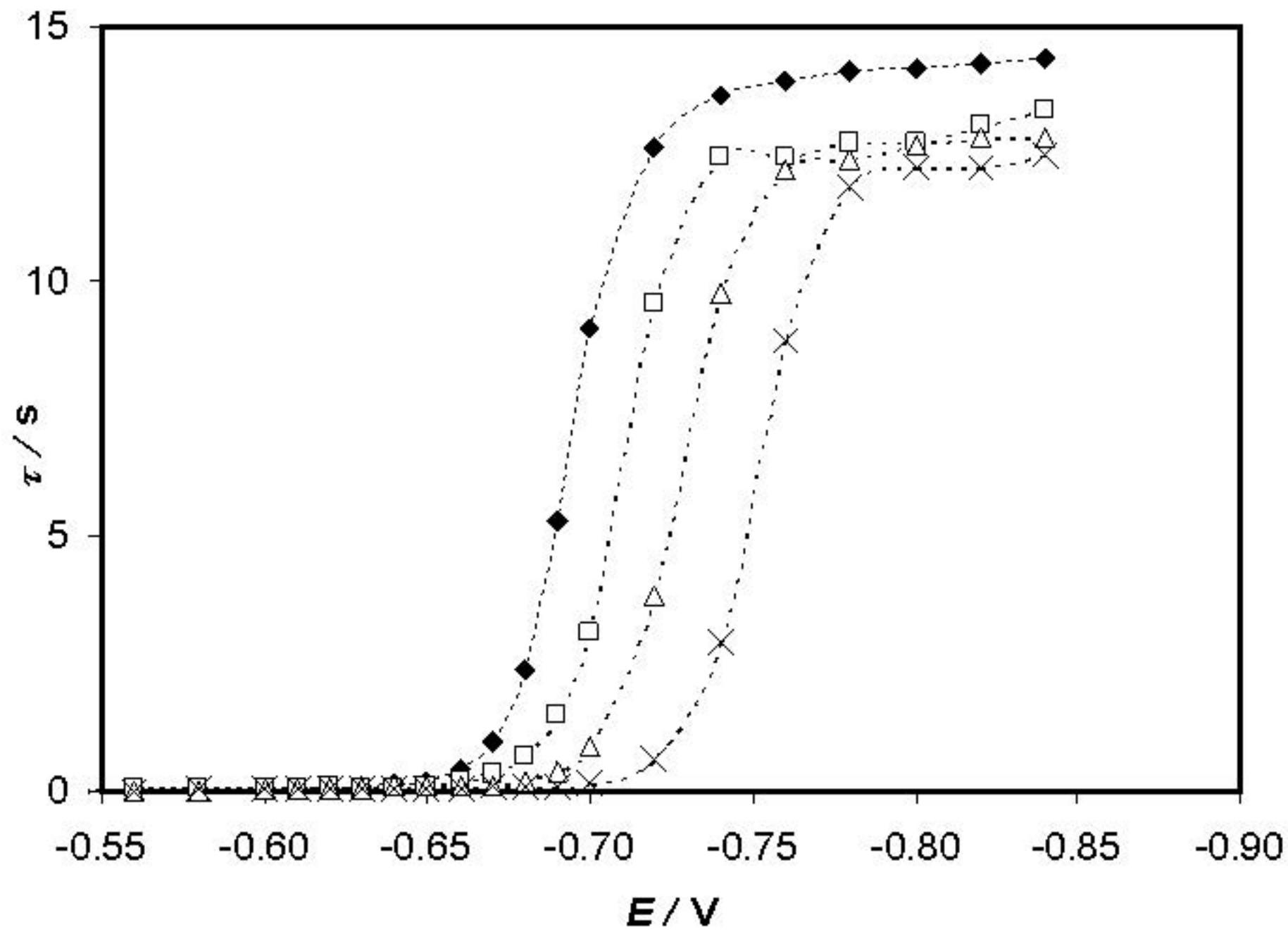


Figure 4

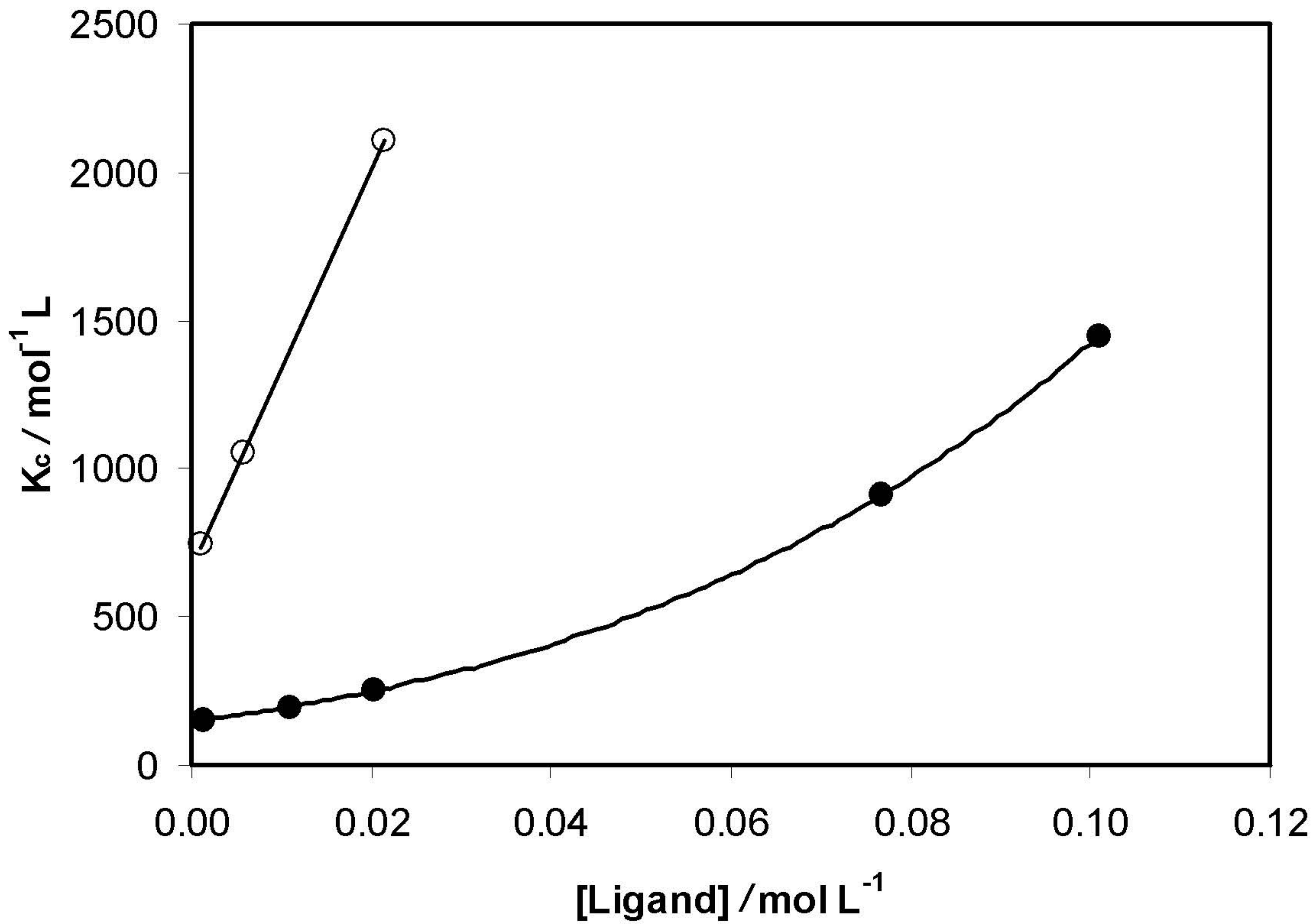


Figure 5

