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Addressing temperature effects on metal chemodynamics studies using stripping electroanalytical techniques. Part 1: Lability of small complexes

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ABSTRACT

Temperature effects on metal speciation dynamics were studied using Stripping Chronopotentiometry at Scanned deposition Potential (SSCP). The temporal and spatial scales of this study are respectively O(10^{-1} s) and O(10^{-5} M), characteristics of the thin mercury film rotating disk, used as working electrode. The lability degree and the association rate constant were evaluated in the temperature interval of 15–40 °C for a significantly non-labile system, cadmium binding by nitrilotriacetic acid, and a quasi-labile system, lead binding by iminodiacetic acid. The results for both systems reveal that the lability of the metal complex significantly increases with temperature. This lability gain results from the thermal augmentation of the association rate constant and the broadening of the diffusion layer thickness.

An evaluation of the metal calibration methodology for SSCP at different temperatures was conducted. It was found that although the variation of diffusion layer thickness can be correctly predicted, changes in standard reduction potential of the metals cannot, thus a calibration must be performed for each temperature studied.

This work constitutes a first step toward the comprehension of the effect of temperature on metal chemodynamics.

1. Introduction

Temperature is a key parameter in electrochemical experiments since it directly affects both the thermodynamics and kinetics of the chemical reactions and the transport of the species from the bulk to the electrode surface.

Thermoelectrochemistry is the branch of electrochemistry that focuses on the variation of the temperature as an independent variable. The increase of temperature is obtained by various means, either directly (heating the working electrode) or indirectly (using microwaves to heat the solution) and the experiments can be performed isothermally or non-isothermally [1]. One interesting analytical aspect is that due to the increased mass transport at high-temperatures higher current signals are obtained, hence lower detection limits [2].

Unfortunately there are very few metal chemodynamics or even metal speciation studies at different temperatures although they are certainly significant as demonstrated recently by Hassler et al. [3] in the study of iron speciation in seawater at 4 °C.

For metal speciation studies the common practice is to work at constant temperature, usually by thermostating the working solution, nevertheless there are some situations where this is not possible, for example, during on-site studies in environmental waters ranging from almost freezing conditions in cold climates to warm waters in tropical regions.

In other situations the objective is to examine the effect of temperature, like in the case of the studies of metal interactions with thermoresponsive polymer nanoparticles in which we are especially interested. In recent years there has been an increasing interest in these particles due to their ability to change their properties, such as dimension, structure, interactions, or aggregation state, in response to external stimuli (temperature, pH, pressure, ionic strength, etc.) [4,5].

Chemodynamic modelling requires both the knowledge of thermodynamic equilibrium parameters and the kinetics of the interconversion of metal complex species. Stripping electroanalytical techniques, like Stripping Chronopotentiometry at Scanned deposition Potential (SSCP) are able to provide thermodynamic and

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kinetic information at the very low concentration levels of metals in environmental samples [6,7]. Effectively the signal of the stripping electroanalytical techniques is determined by the diffusion and/or kinetic fluxes of the various metal species in solution, both depending on the time-scale of the technique and on the intrinsic characteristics of the complexing species.

The main scientific question of this study concerns the effect of temperature on metal complex lability, especially due to the different influence of temperature on some key parameters. For example the thickness of the reaction layer is affected by the ratio of the diffusion coefficient and the association rate constant of the metal, which both increase with temperature.

Additionally there is a methodological question regarding the possibility of performing the calibration at only one temperature followed by complexation studies at different temperatures. This will depend on our ability to predict both the variations of diffusion coefficients (D_M) and standard potential of reduction and amalgamation of the metal species $E°(M^{n+}/M(Hg))$ at different temperatures.

2. Theory

The theoretical basis for stripping chronopotentiometry (SCP), and its use in SSCP are well established [6,7]. In this work we are using a thin mercury film electrode (TMFE) assembled in a rotating disk electrode that has been thoroughly characterised for SSCP experiments [8]. The principles and key equations relevant for the present work, including the temperature effects, are briefly recalled here.

2.1. Metal ions in absence of ligand: SCP limiting current

In stripping chronopotentiometry the number of moles reduced during the deposition step equals the number of moles reoxidized during the stripping step. The limiting transition time (τ^*_M in s) is given by:

$$\tau^*_M = I^*_d t_d / I_s \tag{1}$$

where t_d (s) is the deposition time, I_s (A) the stripping current and I^*_d (A) the limiting value of the deposition current.

I^*_d which by definition is obtained for deposition potentials (E_d) that are sufficiently negative, so that the concentration of metal ions at the electrode surface approaches zero ($c^0_M \to 0$), is given by:

$$I^*_d = (nFAD_M c^*_M)/\delta_M \tag{2}$$

where c^*_M (mol m^{-3}) is the metal concentration in the bulk solution, A is the electrode surface area (m^2), D_M is the diffusion coefficient of the metal ion (m^2 s^{-1}), n is the number of electrons involved in the reduction, F (C mol^{-1}) is the Faraday constant and δ_M (m) is the diffusion layer thickness. For the rotating disk electrode (RDE) the thickness of the diffusion layer is expressed by [9]:

$$\delta_M = 1.61 D_M^{1/3} \omega^{-1/2} \upsilon^{1/6} \tag{3}$$

where ω (s^{-1}) is the angular speed rotation for the RDE ($\omega = 2\pi v_{rot}$, where v_{rot} is the speed of rotation) and υ is the kinematic viscosity of the solution (m^2 s^{-1}).

The variation of the diffusion coefficient of the metal with temperature follows Stokes–Einstein equation given by [10]:

$$D_M = k_B T / 6\pi\eta r_h \tag{4}$$

where k_B (J K^{-1}) is the Boltzmann constant, r_h (m) is the hydrodynamic radius of the diffusion species, T (K) is the temperature and η (Pa s) is the absolute viscosity of the solution, given in Table 1. The variation of viscosity (absolute and kinematic) with temperature was obtained from NIST recommended values [11].

Table 1
Temperature dependence of the absolute viscosity of water (from Kestin et al. [11]) and the diffusion coefficients for Cd^{2+} and Pb^{2+} ions as determined by Eq. (4) using the reference values (a) and (b) from [30,31], respectively.

Temperature (°C)		15	20	25	30	35	40	45
Absolute viscosity (μPa s)		1138	1002	889	796	718	652	595
Diffusion coefficient ($10^{-9} \times$ m^2/s)	Cd	5.56	6.37	7.25$^{(a)}$	8.20	9.23	10.8	11.9
	Pb	6.21	7.13	8.10$^{(b)}$	9.17	10.3	12.0	13.3

The thermal expansion of mercury in the range of temperatures used (288–318 K) is found negligible since it follows the respective variation in density which is −0.54% [12]. Similarly the bulk concentration of metal will be affected by the thermal expansion of water, for which the water density variation is 0.63% (from 288 to 318 K) [13]. Both these volume variations are well below the experimental error of these experiments, so that both the mercury electrode area and volume and the metal concentration are assumed to remain constant within the range of temperatures tested.

From Eqs. (2)–(4) it can be seen that the limiting current depends directly on the temperature through the diffusion coefficient and indirectly through the diffusion layer δ_M dependence on the kinematic viscosity

2.2. Metal ions in absence of ligand: SSCP half-wave potential

The SSCP general equation that describes the relationship between τ and E_d is [7]:

$$\tau = (I^*_d \tau_d / I_s)[1 - \exp(-t_d/\tau_d)] \tag{5}$$

where τ (s) is the transition time, τ_d (s) is the characteristic time constant for the deposition process, which for a TMFE is defined by:

$$\tau_d = V\delta_M/(AD_M\theta) \tag{6}$$

For a TMFE, the volume of the electrode (V in m^3) can be estimated from the charge for reoxidation of the film (Q_{Hg} in C) using Faraday's law and the mercury density:

$$V = M_{w,Hg} Q_{Hg} / 2Fd_{Hg} \tag{7}$$

The parameter θ is the ratio of the surface concentrations ($\theta = c^0_M / c^0_{M^0}$) for the reversible electron transfer reaction, $M^{n+} + ne^- \leftrightarrow M^0$. At a given deposition potential E_d, this parameter is calculated using the following Nernst type equation:

$$\theta = \exp(nF(E_d - E^{0\prime})/RT) \tag{8}$$

where R (J mol^{-1} K^{-1}) the gas constant and $E^{0\prime}$ (V) is a parameter related to the standard potential of reduction for the amalgamation reaction relative to the reference electrode used and the ionic strength of the solution. In SSCP the usual potential parameter is the half-wave potential ($E_{1/2}$) which is a function of $E^0_{M/\{M\text{-}Hg\}}$, temperature, ionic strength, diffusion coefficients of the metal amalgamated and in solution, potential of the reference electrode used and the volume of the electrode, V. The standard potential of amalgam electrodes in aqueous solutions, their temperature coefficients and the activity coefficients of metals in mercury have been reviewed by Mussini et al. [14]

The general scheme of a metal amalgam electrode reaction is:

$$M^{z+} + Hg + ze^- = \{M\text{-}Hg\} \tag{9}$$

and for a TMFE, the simplified version of the equation for the metal amalgamation reduction half-wave potential versus the Ag/AgCl reference electrode can be written as: