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Adsorptive stripping chronopotentiometry (AdSCP).
Part 1: Fundamental features

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Abstract

AdSCP determines a metal ion, M, by reaction with added ligand, L_{ad}, to form a surface active ML_{ad} which is accumulated on an electrode surface, then subsequently reduced. The basic features of adsorptive stripping chronopotentiometric curves for an adsorbed reactant (ML_{ad}) and a dissolved product (M^0) are elaborated in detail. During the accumulation step, practically useful conditions correspond to initial adsorption so strong that limiting adsorption rates are attained, while the surface concentration of the adsorbed complex remains in the linear adsorption regime. Such conditions identify the limiting values of various parameters, e.g. accumulation time, Henry coefficient, and bulk concentration of the target complex. The uncomplexed metal is generally labile with respect to accumulation of ML_{ad}: this feature guarantees equilibrium between ML_{ad} and free M, and thus facilitates rigorous interpretation of the flux, stripping time, and potential expressions. The shape of the potential/ time curve for the stripping step depends on the nature of the diffusive flux of M^0 into the electrode volume. We derive the E/t expression for the general case of a spherical electrode, and specify the limiting cases for a macroelectrode (planar diffusion) and a microelectrode (spherical diffusion), the latter being formally equivalent to the case of an adsorbed product. Expressions for the corresponding dt/dE curves, the area under which corresponds to the stripping transition time, τ, are also given.
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1. Introduction

Electrochemical stripping techniques have great utility for trace metal analysis [1,2]. These methods involve a deposition step, during which the target metal species is accumulated at/in the electrode surface/volume at a constant potential, followed by a stripping step in which the metal is quantified via a potential scan mode (stripping voltammetry, SV) or a constant current mode (stripping chronopotentiometry, SCP). The mode for which interpretation is most straightforward, and for which the theory is most developed [2,3], is that involving reduction of metal species during the deposition step, i.e. the measured species corre-

spond to those that diffuse to the electrode surface and dissociate within the timescale of the measurement. In this context, depletive SCP at scanned deposition potential, SSCP [4], has proved to be especially useful for investigating dynamic metal speciation under a wide variety of conditions: data interpretation is straightforward even in the kinetic regime [5], the entire wave is less affected by induced metal adsorption [6], and there is significant reduction in sensitivity to irreversibility of the electrode reaction involved [7].

Unfortunately however, there are metals for which accumulation of the reduced form, M^0, in the electrode volume is not feasible. This is the case, for example, when the electrochemical reaction of the metal ion is too irreversible, e.g. Ni [8,9], or when the reduced metal does not amalgamate with mercury, e.g. Fe, Al and Cr [10]. In these cases an

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Nomenclature

A	electrode surface area (m^2)	K_H	Henry coefficient (m)
AdSCP	adsorptive stripping chronopotentiometry	$K_{ML_{ad}}$	stability constant for ML_{ad} (dm^3 mol^{-1})
AdSV	adsorptive stripping voltammetry	$K'_{ML_{ad}}$	$K_{ML_{ad}} c^*_{L_{ad}}$
c^*_i	bulk concentration of species i (mol dm^{-3})	$\mathscr{L}$	lability index (dimensionless)
c^0_i	surface concentration of species i (mol dm^{-3})	L_{ad}	added ligand
C_d	double-layer capacitance (F m^{-2})	M	metal
D	diffusion coefficient (m^2 s^{-1})	r_0	radius of electrode (m)
δ	diffusion layer thickness (m)	t_{acc}	accumulation time (s)
E_{acc}	accumulation potential (V)	τ	AdSCP transition time (s)
Γ	surface concentration (mol m^{-2})	τ_{ad}	time constant for steady-state adsorptive accumulation (s)
Γ^{eq}_i	surface concentration of species i at equilibrium (mol m^{-2})	τ_s	time constant for spherical diffusion (s)
I_s	strip current (A)	τ_{ss}	time constant for settling steady-state diffusion (s)
J_i	flux of species i (mol m^{-2} s^{-1})		
$k_{a,ML_{ad}}$	association rate constant for ML_{ad} (dm^3 mol^{-1} s^{-1})	τ_{tr}	time constant for the transient diffusive adsorption process (s)
$k_{d,ML_{ad}}$	dissociation rate constant for ML_{ad} (s^{-1})	$w_{1/2}$	peak half-width (V)

adsorptive stripping mode can be employed, in which the accumulation step involves adsorption of the metal in the form of a surface active complex on the electrode surface, and the stripping (quantification) step involves reduction of the metal complex. Adsorptive stripping voltammetry, AdSV, has thus been widely used for speciation analysis in natural waters. It typically employs a competitive ligand exchange step in which a ligand, L_{ad}, that forms strongly adsorbing complexes with the target metal, is added to the sample, and subsequent measurement of ML_{ad} [11]. Unambiguous quantification of ML_{ad} is essential for metal speciation analysis. So far, the constant current counterpart, AdSCP, has been much less widely exploited [12–20], although some distinct advantages of chronopotentiometric over voltammetric adsorptive stripping have been noted, including a lower influence of surface active impurities [21].

Analogous to SCP, we anticipate that in AdSCP there will be a straightforward quantitative relationship between the signal (i.e. the transition time, τ) and the *amount* of complexed metal adsorbed, whereas this is more involved for various modes of AdSV. Furthermore, the inherent nature of SCP's dt/dE vs E plot means that capacitive current is generally contained in the baseline and does not contribute to the peak [22]: this feature likely explains the ability of AdSCP to 'correct for the large background contribution at carbon electrodes' as compared to AdSV [23]. In SCP the potential scan rate is not constant and is controlled by ongoing faradaic processes: this results in superior resolution over SV in multi-metal systems [24]. The same feature seems to hold for AdSCP since greater resolution of AdSCP over AdSV has been noted [25]. It thus seems timely to analyze the capabilities of adsorptive SCP in detail. Herein we analyze the theoretical background of AdSCP, including the nature of the adsorptive accumula-

tion process and choice of the controlling parameters, e.g. accumulation potential and stripping current. The significance of the role of the lability of free metal ions and the related magnitude of the stability of ML_{ad} and its associated rate constants is elaborated: this knowledge is fundamental for application of AdSCP to speciation analysis. A companion paper [26] addresses the experimental verification and further practical aspects including elementary constraints on the various parameters.

2. Development of the theoretical framework

We consider a sample solution containing the target metal, M, to which we add an excess of ligand, L_{ad}. L_{ad} is chosen such that it has well-defined complexation characteristics with M, and the complexes ML_{ad} are strongly adsorbing on the electrodic surface (usually Hg). The common situation prior to analysis is that *equilibrium* is attained in the bulk sample solution between M and L_{ad}:

$$M + L_{ad} \underset{k_{d,ML_{ad}}}{\overset{k_{a,ML_{ad}}}{\rightleftarrows}} ML_{ad} \tag{1}$$

where $k_{a,ML_{ad}}$ and $k_{d,\ ML_{ad}}$ are the association and dissociation rate constants for ML_{ad}, respectively.

The useful potential range for accumulation in AdSCP is limited: (i) at positive potentials by the decreasing adsorption affinity of the metal complex and/or increasing competitive adsorption from free L_{ad}, and (ii) at negative potentials by reduction of ML_{ad}, or M following dissociation of ML_{ad}. Within these potential limits, the amount of ML_{ad} adsorbed on the electrode surface, $\Gamma_{ML_{ad}}$, depends on the nature of its adsorption isotherm. Here we aim to achieve linear adsorption (Henry regime), and consider initial adsorption to be strong enough to ascertain limiting