Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Electroanalytical Chemistry 589 (2006) 203–211
Journal of Electroanalytical Chemistry
www.elsevier.com/locate/jelechem

Stripping chronopotentiometry at scanned deposition potential (SSCP). Part 8. Metal speciation analysis in gels

Raewyn M. Town [a,*], Lee P. Yezek [b,1], Herman P. van Leeuwen [b]

[a] Department of Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense, Denmark
[b] Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

Received 9 December 2005; accepted 9 February 2006
Available online 23 March 2006

Abstract

In case of a finite negative Donnan potential difference, Ψ_D, metal speciation in a gel is significantly altered as compared to that in the surrounding aqueous medium. For anionic gels (e.g., typical biogels), Ψ_D leads to enhanced concentrations of positively charged species within the gel, and reduced concentrations of negatively charged ones. Thus both the absolute concentrations and the ratios of species are altered. Stripping chronopotentiometry at scanned deposition potential is shown to provide a reliable measure of the stability and lability of metal species in gels. Results are reported for labile, quasilabile and inert metal–ligand systems. Failure to take into account the Donnan partitioning leads to erroneous interpretations on the distribution and lability of species within the gel phase. Translation of the speciation measured within the gel to that in the surrounding medium is involved for chemically heterogeneous systems, e.g., natural waters. The results are of importance for interpretation of analytical signals from gel-integrated sensors and for understanding the behaviour of the different metal species in biogels.

Keywords: Donnan potential; Dynamic metal speciation; Lability; Agarose; Biogel

1. Introduction

Characterisation of metal speciation in aqueous gels is of significance for understanding the behaviour of the different metal species in biogels such as biofilms and cell walls, as well as for the interpretation of signals from analytical speciation sensors that incorporate a gel layer, e.g., diffusive gradients in thin films, DGT [1], and gel-integrated microelectrodes, GIME [2]. In biofilms, the gelating extracellular polymeric substances (EPS) serve to maintain the structure of the cellular aggregates/colonies, and act as a source and sink for nutrients and pollutants [3]. In DGT and GIME the aqueous gel layer provides a well-controlled diffusion medium and also physically protects the active detector body from interfering, larger particles.

The aqueous gels used in DGT and GIME, and the EPS in biofilms, contain a certain amount of sites (groups) that may be negatively charged and thus give rise to a Donnan potential difference, Ψ_D, between gel phase and medium. The magnitude of Ψ_D will increase with decreasing ionic strength and is given by [4]:

$$\Psi_D = \frac{RT}{zF}\operatorname{asinh}\left(\frac{\rho_g}{2zFc}\right) \quad (1)$$

where $z = z_+ = z_-$ is the valence of the symmetrical excess background electrolyte with bulk concentration c, ρ_g is the volume charge density due to fixed charge groups in the gel, and other constants have their usual meaning. The magnitude of Ψ_D influences the equilibrium partitioning of all ions between the gel phase (with concentration c_g) and the electrolyte solution (with concentration c^*). The

* Corresponding author. Tel.: +45 65502503; fax: +45 66158780.
E-mail address: rmt@chem.sdu.dk (R.M. Town).
[1] Present address: Institut für Geotechnik, Eidgenössische Technische Hochschule, ETH Hönggerberg, CH-8093 Zürich, Switzerland.

0022-0728/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2006.02.008

Nomenclature

c	concentration (mol dm^{-3})
$\bar{\delta}$	average diffusion layer thickness (m)
δ_g	gel layer thickness (m)
D	diffusion coefficient (m^2 s^{-1})
DC	direct current
DGT	diffusive gradients in thin films
DP	differential pulse
ε	D_{ML}/D_M
E_d	deposition potential (V)
$E_{d,1/2}$	half-wave deposition potential (V)
EPS	extracellular polymeric substances
g	subscript to denote a gel phase parameter
I	ionic strength (mol dm^{-3})
I_d^*	SCP limiting deposition current (A)
I_s	stripping current (A)
J	flux (mol m^{-2} s^{-1})
k_d	complex dissociation rate constant (s^{-1})
K	stability constant (dm^3 mol^{-1})
$\mathscr{L}$	lability parameter (dimensionless)
PCA	pyridine-2-carboxylic acid
PDCA	pyridine-2,6-dicarboxylic acid
Π_D	Donnan partitioning (concentration factor)
Ψ_D	Donnan potential difference (V)
r_0	radius of microelectrode (m)
ρ_g	volume charge density in the gel (C m^{-3})
SSCP	stripping chronopotentiometry at scanned deposition potential
SSV	stripping voltammetry at scanned deposition potential
SW	square wave
τ*	SSCP limiting transition (stripping) time (s)
τ_d	potential-dependent characteristic time constant of the SCP deposition process
τ_{ss}	time constant for attainment of steady-state (s)
t_d	deposition time (s)
z	ion valency

Donnan partitioning, Π_D, can be described by a Boltzmann factor [5]:

$$\Pi_D = \frac{c_g}{c^*} = \exp\left(\frac{-zF\Psi_D}{RT}\right) \quad (2)$$

which shows that for anionic gels, the concentration of all positively charged species within the gel will be enhanced relative to the bulk solution, and that of all negatively charged species reduced. The actual difference in concentration factors for various charged species will thus depend on Ψ_D, e.g. for a Ψ_D of -30 mV, the Π_D is more than 10 for the divalent M^{2+}. In addition, the amount/distribution of complex species in the gel depends on the free ligand concentration which may be altered (lowered) by the Donnan potential, and which in turn may invoke a further change in pH, with additional consequences for the metal speciation. Thus the analytical signal from a sensor that incorporates a gel layer reflects the Donnan partitioning (of cationic and anionic species), as well as the diffusive mobility and lability of metal species within the gel phase. Quantification of these effects is fundamental to correct interpretation of sensor signals and to understanding the role of biofilms in aquatic ecosystems and bioavailability to biota in such aggregates.

Here we apply stripping chronopotentiometry at scanned deposition potential (SSCP) to metal speciation analysis in an agarose gel for a range of Donnan potentials, for labile and quasilabile systems, and for metal species of different charge (M^{2+}, ML^+, ML^0). SSCP, under depletive stripping conditions, provides a straightforward quantitative relationship between the amount of metal accumulated during the deposition step and the analytical signal. The slow rate of oxidation applied in this SSCP mode renders it practically immune to adsorption of the electroactive species [6,7], it has a lower requirement for excess ligand in the sample solution [6,8] and greater resistance to both irreversibility in the electrochemical oxidation [9,10] and interference from intermetallic compounds [11]. These features allow the thermodynamic and kinetic characteristics of the metal species to be determined unambiguously from the SSCP wave parameters (limiting stripping time, τ^*, and shift in half-wave deposition potential, $\Delta E_{d,1/2}$) [7,12–14]. SSCP has greater sensitivity, and provides greater resolution in multi-metal systems than does depletive DC-SSV [15], whilst the widely used transient voltammetric techniques, DP and SW, are affected by interferences due to induced metal ion adsorption [16] and ligand saturation during stripping [8,17].

The concentration factors and speciation, as ensuing from τ^* and $\Delta E_{d,1/2}$, measured within the gel, are compared with those calculated for the pertaining Donnan potential. Strategies are proposed for relating the speciation measured within the gel to that in the surrounding aquatic medium.

2. Experimental

2.1. Apparatus

The potentiostat was an Ecochemie μAutolab with electrometer input impedance of >100 GΩ. The auxiliary electrode was glassy carbon, and the reference electrode was Ag|AgCl|KCl(sat). The working electrode was a mercury-coated iridium microelectrode: measurements were performed in the absence and presence of an agarose gel layer. The radius of the hemispherical mercury droplet was