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Application of permeation liquid membrane and scanned stripping chronopotentiometry to metal speciation analysis of colloidal complexes

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Abstract

The potential of permeation liquid membrane (PLM) to obtain dynamic metal speciation information for colloidal complexes is evaluated by measurements of lead(II) and copper(II) complexation by carboxyl modified latex nanospheres of different radii (15, 35, 40 and 65 nm). The results are compared with those obtained by a well characterized technique: stripping chronopotentiometry at scanned deposition potential (SSCP). Under the PLM conditions employed, and for large particles or macromolecular ligands, membrane diffusion is the rate-limiting step. That is, the flux is proportional to the free metal ion concentration with only a small contribution from labile complexes. In the absence of ligand aggregation in the PLM channels, good agreement was obtained between the stability constants determined by PLM and SSCP for both metals.

Keywords: Colloidal dispersions; Dynamic speciation; Lability; Permeable liquid membrane; Stripping chronopotentiometry at scanned deposition potential

1. Introduction

In natural aquatic systems metal ions form stable complexes with a large variety of dissolved inorganic and organic ligands, such as natural macromolecules, colloids and particles, which may be taken up by microorganisms [1,2]. The importance of the interconversion between the different metal species and their kinetic characteristics, e.g. reactivity, mobility and bioavailability [3,4], has been increasingly recognized as a key features of the environment since natural aquatic systems are subject to changing conditions and practically never reach chemical equilibrium. A quantitative understanding of these relationships requires the dynamic characterization of trace metal ion speciation [2,5,6].

To facilitate the dynamic interpretation of these systems a lability criterion was developed for the common practical cases [7]. The lability concept is used to estimate the contribution of the metal species to the overall flux toward the consuming interface. Metal complex systems are classified as static, if they cannot dissociate in the time scale of the technique, and dynamic, if they frequently dissociate and reassociate within the measurement time scale. The contribution of dynamic complexes to the overall metal flux depends on the relative values of the diffusive and kinetic fluxes, which can range from fully labile (diffusion control) to non-labile (kinetic control).

Dynamic metal speciation analysis remains a challenging problem since very few techniques combine the potential to perform dynamic speciation and high sensitivity [8]. Among those are the thin layer separation techniques, such as permeation liquid membrane (PLM) [9–11], and the electrochemical stripping techniques, especially the newly developed stripping chronopotentiometry at scanned deposition potential (SSCP) [12–14]. These techniques are characterized by their: (i) response time, determined by the thickness of the diffusion layer, and (ii) accumulation time, i.e., the period of time over which species are accumulated in the sensor prior to the quantification [15]. Lability is an operational parameter that depends on the response time

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scale of the analytical technique, and determines the dynamic (i.e., labile and mobile) metal species that it will measure.

2. Theory

In case of colloidal dispersions it is necessary to consider the physicochemical nature of the ligand distribution. A novel dynamic metal speciation theory for colloidal dispersions was recently presented [16] in which the ligands are localized on the surface of the colloidal particles. Since the concentrations of ligand and metal are confined by the particle geometry, the reaction between M and ML can be severely limited by diffusion. As a consequence, the finite rate of association/dissociation kinetics of the volume complexation reaction (the dynamic criterion), and the interfacial flux of free metal to a macroscopic surface due to the dissociation of complex species (the lability criterion) are effectively modified.

The apparent rate constants of complex formation and dissociation in colloidal ligand dispersions, k_a^* and k_d^*, are given by [16]:

$$k_a^{*'} = \frac{k_a'}{(1 + k_a'(4\pi a D_M c_p)^{-1})} \quad (1)$$

$$k_d^* = \frac{k_d}{(1 + k_a'(4\pi a D_M c_p)^{-1})} \quad (2)$$

where a is the radius of the supposedly spherical colloidal particle, c_p is the particle number concentration, D_M is the diffusion coefficient of the free metal, and k_a and k_d are the rate constants of complex formation and dissociation in a homogeneous solution of the same ligand.

The system is dynamic if the rates for the volume reactions are fast on the experimental time scale, t:

$$k_d^* t, \quad k_a^{*'} t \gg 1 \quad (3)$$

Under conditions of ligand excess we can define:

$$k_a^{*'} = k_a^* c_{L,T} \quad \text{and} \quad K' = \frac{k_a^{*'}}{k_d^*} = K c_{L,T} \quad (4)$$

where $c_{L,T}$ is the total concentration of the ligand.

The lability index, L^*, under steady state transport conditions is given by [17]:

$$L^* = \frac{\bar{d}}{(\mu \varepsilon K')} \quad (5)$$

where $\bar{d}$ is the thickness of the diffusion layer (which for a spherical electrode is $(1/\delta + 1/r_0)^{-1}$, where δ is the mean diffusion layer thickness and r_0 is the electrode radius, and for the PLM is $D_M c_{M,T}^{so}/\bar{J}_{so}$, where $c_{M,T}^{so}$ and $\bar{J}_{so}$ are the total metal and the average flux in the source solution, respectively), μ is the thickness of the reaction layer boundary ($\mu = (D_M/k_a')^{1/2}$), and $\varepsilon = D_{ML}/D_M$ (for $L^* \gg 1$ the complex is labile, and for $L^* \ll 1$ the complex is non-labile).

The PLM system for metal ion transport consists of a hydrophobic membrane, impregnated with an organic solvent containing a selective complexing carrier [18], which separates a source solution containing the target metal species and a strip solution with a complexing agent that is much stronger than the carrier. The speciation analysis is based on the magnitude of the metal flux from the source solution to the hydrophobic membrane and to the strip solution. There are two limiting situations regarding the flux: (i) diffusion in the source solution is rate limiting, and both the free metal and the labile complexes contribute to the flux; and (ii) the diffusion across the membrane is governing the flux, and only the free metal ion is measured.

The performance of the PLM device can be checked by plotting the time dependence of the accumulation factor, $F(t)$. This factor can be defined as:

$$F(t) = \frac{c_{M,T}^{st}(t)}{c_{M,T}^{so}} \quad (6)$$

where $c_{M,T}^{st}(t)$ is the metal concentration in the strip solution at time t. The experimental mean flux can be deduced from the slope of the preconcentration factor versus time.

Under ligand excess conditions and when M is complexed in the source solution the total flux, $\bar{J}_t$, is modified as follows [10]:

$$\text{for inert complexes :} \quad \frac{1}{\bar{J}_t} = c_{M,T}^{so}\left(\frac{\bar{\delta}_{so}}{D_M} + \frac{l}{D_{MC}^{m} K_D}\right)\alpha_{so} \quad (7)$$

$$\text{for labile complexes :} \quad \frac{1}{\bar{J}_t} = c_{M,T}^{so}\left(\frac{\bar{\delta}_{so,ML}}{D_{so}} + \frac{l}{D_{MC}^{m} K_D}\alpha_{so}\right) \quad (8)$$

where l is the membrane thickness, K_D is $K_p c_{C,T}^{m}$ (K_p is the partition coefficient of M between the organic and the source phase, and $c_{C,T}^{m}$ is the total carrier concentration in the membrane), $\bar{\delta}_{so}$ and $\bar{\delta}_{so,ML}$ are the effective thicknesses of the diffusion layer in the absence and presence of complex ML, respectively, D_{MC}^{m} is the diffusion coefficient of the complex MC in the membrane, $\overline{D_{so}}$ is the mean diffusion coefficient of metal species in the source solution ($\bar{D} = D_M(1 + \varepsilon K')/(1 + K')$) and α_{so} is the degree of complexation of M ($\alpha_{so} = c_{M,T}^{so}/c_M^{so} = 1 + K'$), where c_M^{so} is the concentration of the free metal ion in the bulk source solution.

Few studies have been made on PLM application to trace metal elements analysis in natural waters and still fewer studies for metal speciation studies under natural water conditions [19,20]. This technique has shown promising results in speciation analysis of small metal complexes [21–23].

Stripping chronopotentiometry is a technique that is relatively insensitive to organic matter adsorption interferences [24,25] and possesses a detection limit that is comparable to that of pulsed stripping voltammetries. A rigorous equation is available for the full wave in the kinetic current regime for the complete depletion mode of scanned stripping chronopotentiometry (SSCP) [26]. Using this expression, Pinheiro and van Leeuwen [14] showed that the analytical signal, τ, reflects the magnitude of the original flux independent of its nature (i.e., diffusion controlled or kinetically controlled). Therefore the shift in the half-wave deposition potential, $\Delta E_{d,1/2}$, (analogous to the