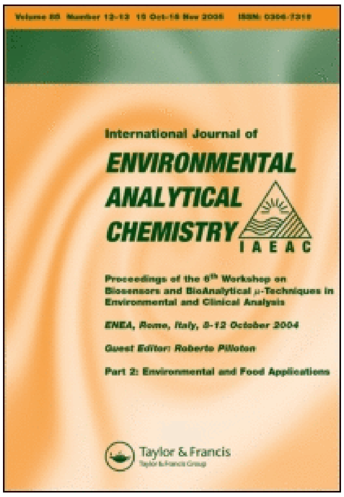

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METAL SPECIATION IN POLYELECTROLYTIC SYSTEMS BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

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The differential pulse anodic stripping voltammetry (DPASV) of a number of metal/polyelectrolyte complexes is studied, taking into account the (large) differences between the diffusion coefficients of the free and complexed metal. Zinc polymethacrylate, cadmium polymethacrylate and zinc polyacrylate systems are found to be labile under stripping voltammetric conditions. Over a wide range of metal-to-ligand ratios, their DPASV peaks are successfully analyzed in terms of a mean diffusion coefficient $\bar{D}$. This $\bar{D}$ reflects the speciation of the metal over free and complexed form as governed by the stability of the metal/polyanion complex. For lead and cadmium polyacrylates, the variation of the DPASV peak height with polyion concentration is more involved since it cannot be explained on the basis of differences in diffusion coefficients and finite rates of complex association/dissociation.

KEY WORDS: Heavy metals, polycarboxylic acids, voltammetry, speciation.

INTRODUCTION

Metal speciation is a prerequisite in environmental chemistry. It enables the assessment of bio-available fractions of heavy metals in natural waters and soil solutions.[1] Voltammetric methods are among the most popular in environmental metal speciation studies. In principle, they are suited to distinguish between different chemical forms of most of the important trace metals.[2,3] For example, stripping voltammetry is frequently practised in heavy metal speciation procedures, in order to determine the distribution of metal ions over the "free" and the "complexed" forms.[4-6] Yet in many cases the exact interpretation of experimental results is very complicated, if not impossible, and a much better theoretical basis for stripping voltammetry of metal complexes is badly needed.

For labile metal complexes, any metal ion frequently flip-flops between the

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bound and the free state within the time scale of the experiment. In the case of macromolecular labile complex with a diffusion coefficient much smaller than that of the free metal ion, the voltammetric current will be controlled by the mean diffusion coefficient of the metal complex system. Such a mean diffusion coefficient $\bar{D}$ is defined as:

$$\bar{D} = c_M^* \cdot D_M / c_T^* + c_{ML}^* \cdot D_{ML} / c_T^* \qquad (1)$$

and for the case of semi-infinite linear diffusion, the current is proportional to $\bar{D}^{1/2} \cdot c_T^*$. For systems which are not labile, voltammetry is still in its infancy since it has long been lacking a rigorous theory which considers the different diffusion coefficients of the species involved and the finite rates of interconversion. Only recently some attempts at developing such a theory were made.[7-10] Van Leeuwen[10] has discussed the interpretation of voltammetric polyelectrolyte—metal ion titrations in terms of the homogeneous kinetic effects and diffusion coefficients, indicating that the electrochemical lability of the systems changes with the ratio between the concentrations of metal and ligand. In the case of natural organic complexing agents (humic and fulvic acids, mainly), the interpretation of the voltammetric current-potential response curves, and thus the physico-chemical description of the complex formation, is seriously affected by the macromolecular and polyfunctional character of these main constituents of organic matter in ecosystems. Furthermore, the organic ligands occurring in nature are not homogeneous with respect to thermodynamics and kinetics of metal binding as well as diffusion coefficients[11] and therefore they are not very suitable in the stage of verifying the recently developed theory. A better choice is a homofunctional synthetic polyacid such as polyacrylic acid (PAA) or polymethacrylic acid (PMA) with a fairly sharp molecular weight distribution.

To investigate the effect of the macromolecular character of polycarboxylate ligands on the voltammetric response to the complexation with heavy metals, the systems Cd, Pb, Zn/PAA, PMA have been studied by differential pulse anodic stripping voltammetry (DPASV) at metal concentration levels around $1\ 10^{-7} - 1\ 10^{-6}\,\mathrm{mol\,l^{-1}}$ and with $0.1\,\mathrm{mol\,l^{-1}}$ KNO_3 as supporting electrolyte. From a methodological point of view, DPASV is not the preferable technique, but it allows extremely low metal-to-ligand ratios which is quite advantageous for two reasons. First, theory is only available for the case of large excess of ligand, and second, the binding parameters and the diffusion coefficient of the ligand may be considered to be independent of the very small amount of metal bound. Taking into account that DPASV is well applied in today's speciation practice and that some orientational data on the pulse polarography of these systems are already available, it seems timely to initiate the study of stripping voltammetry of metal/polyelectrolyte complexes.

MATERIALS AND METHODS

Polyacrylic Acid (PAA) and Polymethacrylic Acid (PMA)

The polyacrylic acid (PAA) and polymethacrylic acid (PMA) solutions were obtained from BDH. The average molecular masses, according to BDH, 230,000 and 26,000 grs mol^{-1}, respectively. Stock solutions of ca. 0.1 mol l^{-1} (in monomers) were prepared by dilution with water. Their total number of carboxylic groups were determined by conductometric acid-base titration. The intrinsic dissociation constant of PAA and PMA appeared to be $10^{-4.7}$ and $10^{-4.9}$, in mol l^{-1} units, respectively. The diffusion coefficients of PAA and PMA, as calculated from literature data,[12] are approximately 10^{-7} and 1.5 10^{-7} cm^2 s^{-1}, respectively, for the molecular mass versions used.

Other Reagents

All other reagents used were analytical grade. KOH was used for the partial neutralization of the polyacid solutions. KNO_3 was applied as supporting inert electrolyte, at a concentration of 0.1 mol l^{-1}. Solutions of $Cd(NO_3)_2$, $Pb(NO_3)_2$ and $Zn(NO_3)_2$ were used at the levels 1 10^{-7} – 1 10^{-6} mol l^{-1}. The diffusion coefficients of uncomplexed Cd^{2+}, Pb^{2+} and Zn^{2+} are all on the level of 10^{-5} cm^2 s^{-1}. Millipore Super-Q water was employed in all experiments. After degassing traces of CO_2, the water had a conductivity less than 0.5 μS cm^{-1}.

Differential Pulse Anodic Stripping Voltammetry (DPASV)

The DPASV voltammograms were obtained with an EG&G PAR Model 174A polarographic analyzer, attached to a VA 663 Metrohm electrode system through a home-made interface. The reference electrode, to which all potentials are referred, was Ag/AgCl, NaCl(sat.). The pulse duration was 40 ms and the pulse height was 25 mV. The deposition potentials were −800 mV for Pb^{2+} and Cd^{2+}, and −1400 mV for Zn^{2+} containing sample solutions. The preelectrolysis time and the rest period observed were 1 and 0.5 min, respectively. The scan rate in the stripping step was 10 mV s^{-1}. Teflon cells were used in all the measurements, which were made at 25 °C. Purified nitrogen was used for deaeration and blanketing of the sample solutions.

Procedure

Solutions of PAA and PMA were partially neutralized to a certain degree of neutralization α_n. Aliquots of these solutions were pipeted into the metal ion solutions, and the DPASV voltammograms were recorded. In line with the basic goal of this work, experiments were continued till very large excesses of ligand over metal, typically of the order of 100:1, were achieved. One should realize this when considering the resulting “titration” curves. Peak currents were corrected for dilution due to addition of polyelectrolyte solution, so that they all refer to the same total metal concentration.

Calculations

In order to fit the experimental results to theoretical predictions, a FORTRAN program was developed. The program fits peak current data from an ASV ligand titration of a metal solution. It is formulated in terms of a normalized peak current, ϕ, defined as:

$$\phi = I_p \text{ in the presence of ligand}/I_p \text{ in the absence of ligand.} \tag{2}$$

Assuming lability, ϕ is fitted to the postulated functionality:

$$\phi = (\bar{D}/D_M)^p = (1 + \varepsilon \cdot K \cdot c_L^*)^p/(1 + K \cdot c_L^*)^p \tag{3}$$

where the parameter p is related to the nature of the mass transport during the pre-electrolysis step. It may be expected to be between 0.50 (semi-infinite linear diffusion) and 0.67 (laminar convective diffusion). As before, ε and K are given by:

$$\varepsilon = D_{ML}/D_M \tag{4}$$

$$K = c_{ML}^*/c_M^* \cdot c_L^*. \tag{5}$$

The notion K' is often used in cases of large excess of ligand:

$$K' = K \cdot c_L^* \quad (c_L^* \gg c_{ML}^* + c_M^*). \tag{6}$$

The value of K for infinitely small polyionic charge density, usually found by some extrapolation procedure, is indicated by K(int). It denotes the intrinsic stability constant, free from polyelectrolytic binding effects.

Three options are available in the fitting process:

a) K, ε and p are unknown; input: some guessed values for K, ε and p to speed up the computation.

b) K and ε are unknown, p is fixed; input: guessed values for K and ε, and the fixed values of p.

c) K and p are unknown; ε is fixed; input: guessed values for K and p, and the fixed value of ε.

A basic element of the program is the subroutine ZXMIN, taken from the IMSL library.[13]

RESULTS AND DISCUSSION

The Zn/PMA System

Previous normal pulse polarographic investigations[14, 15] showed a linear relation-

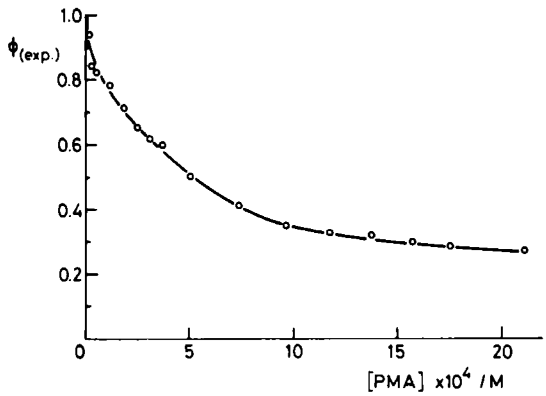

Figure 1 Experimental ϕ values as a function of the PMA concentration for the Zn/PMA system, at $\alpha_n = 0.8$.

ship between limiting current and $t_{\mathrm{pulse}}^{-1/2}$, and a pulse time-independent character of $E_{1/2}$. These observations indicate labile behaviour of the system under pulse polarographic conditions. Log K(int) values of ca. 1.1 were obtained from polarographic data.

In Figure 1 ϕ(exp), the experimental value of the normalized limiting current, is plotted as a function of the PMA concentration for the Zn/PMA system in a DPASV titration. The fit of the ϕ(exp) vs. [PMA] dependence was made using Eq. (3), which is for the labile case. In the calculations the guessed values for K, ε and p were of the order of (magnitude of) 10^4, 10^{-2} and 0.5, respectively. The option (a) in the fitting gives unrealistically small ε values (ca. 10^{-12}), the option (b) for a fixed $p = 0.5$ (assumed from Ref. 10) gives K values of $7\ 10^3$ and $7.6\ 10^3$ for two independent series, while option (c) with a fixed $\varepsilon = 0.019$ (assumed from Ref. 15) gives realistic values with K in the range $4.7\ 10^3$–$7\ 10^3$ and p in the range 0.52–0.59, and with very favourable correlation coefficients ($r^2 = 0.9933$).

The Cd/PMA System

Previous pulse polarographic investigations[14] showed characteristic features: (a) K' values as obtained from $E_{1/2}$ much lower than those evaluated from ϕ, (b) a dependence of ϕ on the initial potential, suggesting adsorption of the metal ion induced by adsorption of PMA in the period prior to pulse application. The adsorption of the PMA complexes occurs especially in the potential region around the potential of zero charge.

Under ASV conditions, with a preelectrolysis potential of −800 mV the electrode carries such a negative charge that PMA adsorption is prevented by electrostatic repulsion and therefore the ASV data for the system can be consistently analyzed by taking into account homogeneous chemical kinetics only. In Figure 2 ϕ(exp) is plotted as a function of the PMA concentration for the Cd/PMA system. Analysis of the ASV data assuming lability by the three above-

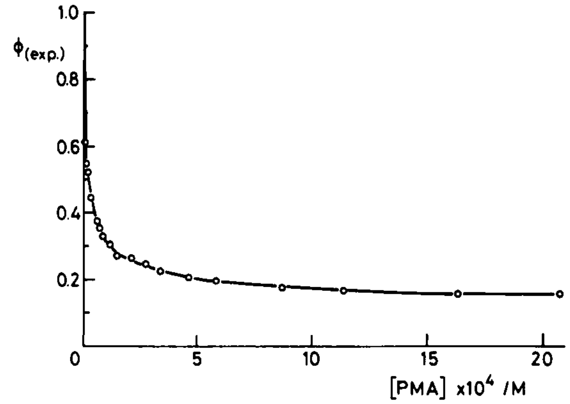

Figure 2 Experimental ϕ values as a function of the PMA concentration for the Cd/PMA system, at $\alpha_n = 0.8$.

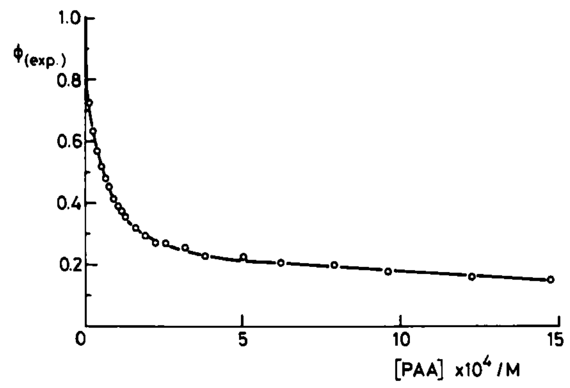

Figure 3 Experimental ϕ values as a function of the PAA concentration for the Zn/PAA system, at $\alpha_n = 0.8$.

mentioned options give K values inside the range 1.3 10^5–3.2 10^5. By fixing $p = 0.5$, ε values of ca. 0.029 are obtained, while fixing $\varepsilon = 0.019$, $p = 0.45$ and $K = 1.7\ 10^5$ are obtained.

The Zn/PAA System

The system Zn/PAA appeared to be polarographically labile,[16] with $\log K(\text{int})$ values of ca. 1.7, obtained from polarographic data.[15]

In Figure 3 ϕ(exp) is plotted as a function of the PAA concentration for the Zn/PAA system at $\alpha_n = 0.8$. Analysis of the ASV data, under such assumption, by the three above-mentioned options give K values in the range 5.4 10^4–6.1 10^4. By fixing $p = 0.5$, $\varepsilon = 0.012$ is obtained, while by fixing $\varepsilon = 0.019$, $p = 0.531$.

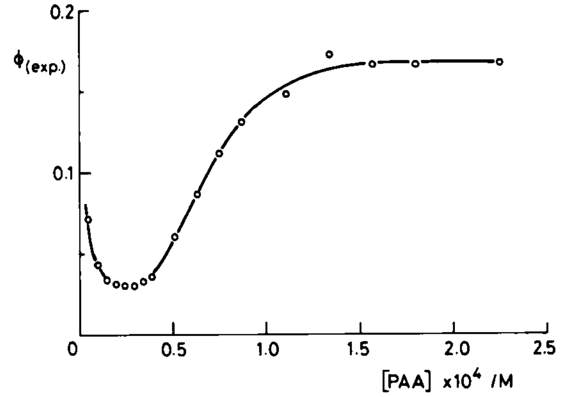

Figure 4 Experimental ϕ values as a function of the PAA concentration for the Pb/PAA system, at $\alpha_n = 0.3$.

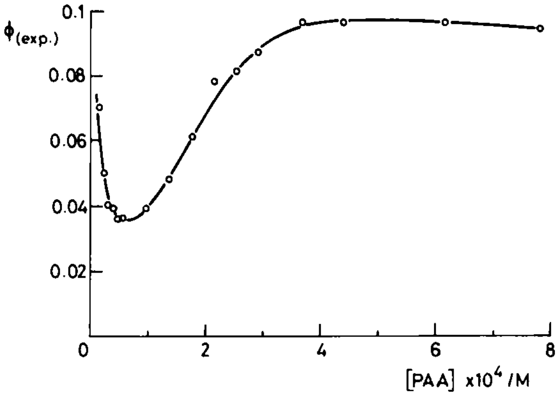

Figure 5 Experimental ϕ values as a function of the PAA concentration for the Pb/PAA system, at $\alpha_n = 0.5$.

The Pb/PAA System

Previous polarographic results[14] showed that the Pb/PAA system could not be analyzed on the basis of the assumption of labile behaviour. Experimental data indicated that the Pb/PAA system, under the given polarographic conditions, is an example of a system which is dynamic but not labile; this means that the measured currents are strongly influenced by the complex association/dissociation kinetics in the solution. DPASV experiments, made at different conditions, also shows more involved behaviour. Figure 4 shows ϕ(exp) plotted as a function of the PAA concentration, for the Pb/PAA system, at $\alpha_n = 0.3$ and Pb^{2+} 2.5 10^{-6} mol l^{-1}. Figure 5 shows the same representation but obtained at $\alpha_n = 0.5$. Normal shapes are obtained at the Pb^{2+} 2.5 10^{-7} mol l^{-1} level at $\alpha_n = 0.5$, but again anomalous shapes at 5 10^{-7} mol l^{-1} level at $\alpha_n = 0.3$. In all anomalous cases the curves cannot be explained in terms of Eq. (3) since the system is not labile. Attempts to describe the minimum in the ϕ vs. c_L^* curve by considering finite complex association/dissociation rate constants were not successful either. It seems that some other effect is playing a role, and therefore additional experiments would be necessary to clarify the behaviour of this particular system.

The Cd/PAA System

The complex Cd/PAA has been shown to behave as a labile system on the pulse polarographic time scale,[15] with $\log K(\text{int})$ values of ca. 2.1. However, plots of $\phi(\text{exp})$ as a function of the PAA concentration for the Cd/PAA system at $\alpha_n = 0.8$ and Cd^{2+} 2.5 10^{-6} mol l^{-1} show anomalous shapes similar to those obtained for the Pb/PAA system. As a consequence, the stripping voltammetric data cannot be explained in terms of labile complex behaviour.

CONCLUSIONS

The systems Zn/PMA, Cd/PMA and Zn/PAA appear to be voltammetrically labile under the DPASV conditions employed. On the contrary, the systems Pb/PAA and Cd/PAA are more complicated, and additional experiments will be necessary to clarify and understand their behaviour. For the above-mentioned labile systems, the fit to the theoretical functionality is very good. In terms of the resulting stability constant and the resulting power of $\bar{D}$, indicated by the p value, the results seem most satisfactory. One of the striking observations is that, for not too strong but labile complexes, the value of D_{ML} (much smaller than D_M) is not really very important in a relatively wide range of metal-to-ligand ratios. Note that this is basically different from saying that the complex does not contribute to the current! This fact is understandable since in the major part of the curve, the free metal is the primary factor determining the mean diffusion coefficient of the system, whereas the voltammetric response is determined by $\bar{D}$ and the total metal concentration. The obtained results also show that fitting K, ε and p without any fixed value, yields good K and p values but often very low ε values, corresponding with a continually decreasing experimental curve. By fitting the curves with fixed ε values, obtained from previous polarographic studies,[12,14,15,16] good K values are obtained and, furthermore, the resulting p values close to 0.5 agree with previous theoretical assumptions.[10] The general conclusion may be drawn that the stripping voltammetry of metal/polyelectrolyte complexes is well understood, provided they are electrochemically labile.

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