
**STRIPPING VOLTAMMETRY OF ZINC/POLYACRYLATE
COMPLEXES: INFLUENCE OF MOLAR MASS***

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Dedicated to the memory of our colleague and friend Dr Jiří Tenygl.

Differential pulse anodic stripping voltammetry (DPASV) has been applied to complex systems of zinc(II) and polyacrylic acid (PAA) for various molar masses of the polyacid. The Zn/PAA complex is voltammetrically labile over the whole range of metal-to-ligand ratios. Analysis of the data in terms of a mean diffusion coefficient, which decreases with increasing molecular mass, yields a consistent picture with molar mass-independent complex stabilities. The speciation of Zn(II) in such a polyelectrolyte system varies with the concentration of carboxylate groups and with the overall charge of the PAA, but it is invariant with the polyionic molar mass.

Knowledge of the speciation of metals (i.e., their distribution over different physico-chemical forms) is essential to the understanding of many practical properties of natural water samples. Extensive lists of references to studies of heavy metal speciation in systems with macromolecular ligands such as humic acids, polysaccharides, proteins, etc. can be given^{1,2}. Already in the early days of polarography, the Czechoslovak school of Heyrovský³ drew attention to the specific potentialities of voltammetric techniques for the characterization of all kinds of homogeneous complexation reactions of electroactive metal ions. Nowadays voltammetry has become a most important tool in environmental metal speciation studies. This is especially true for stripping voltammetry (SV) since this technique allows direct speciation measurements in samples with metal ion concentrations down to the sub-ppb levels. However, the use of stripping voltammetry involves a pre-electrolysis as an essential first step. During this step, the mass transport conditions are generally less well-defined than in a purely diffusion-controlled direct voltammetric experiment. With labile complex systems, the speciation essentially runs through the analysis of the overall mean

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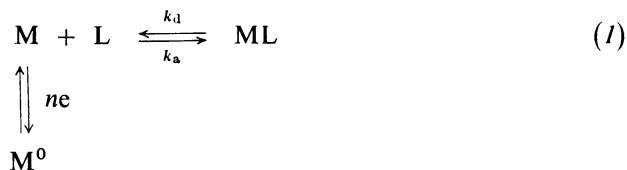
diffusion coefficient (\bar{D}) and therefore any uncertainty in the relationship between response and diffusion coefficient affects the computed speciation.

Operationally, one can measure a given type of system by SV under conditions of different metal-to-ligand ratios, and fit the resulting response curve to the best possible relation with \bar{D} to some power. The data available indicate that this semi-empirical procedure works satisfactorily well within experimental error for a number of labile systems, e.g. Zn/PMA and Cd/PMA (ref.⁴).

The aim of the present paper is to extend our systematic stripping voltammetric study of metal/polyelectrolyte complexes to systems with different polyionic diffusion coefficients, while keeping the complexation properties the same. This can be realized by varying the molar mass of the polyacid involved. We have selected some Zn/PAA systems with different molar masses, and studied these by differential pulse anodic stripping voltammetry (DPASV) for different degrees of neutralization of the PAA at a metal concentration level of $10^{-6} \text{ mol l}^{-1}$. The use of a stripping technique and a low metal ion concentration allows the achievement of full complexation conditions at sufficiently low ligand concentrations.

THEORETICAL

The complexation scheme in which an electroactive metal ion (M) associates with a ligand or site (L) to form an electroinactive complex (ML) can be presented as:



where M^0 denotes the metal atom and k_a and k_d are the association and dissociation rate constants, respectively. The complexation equilibrium in the bulk is expressed by the stability K :

$$K = \frac{c_{\text{ML}}^*}{c_{\text{M}}^* c_{\text{L}}^*}, \quad (2)$$

where c_{M}^* , c_{L}^* and c_{ML}^* denote the bulk concentrations of M, L and ML, respectively. When a large excess of ligand is present ($c_{\text{L}}^* \gg c_{\text{T}}^* (= c_{\text{M}}^* + c_{\text{ML}}^*)$), the association becomes quasi-monomolecular with a rate constant

$$k'_a = k_a c_{\text{L}}^*. \quad (3)$$

The corresponding stability K' is then the ratio between bound and free metal

$$K' = \frac{k'_a}{k_d} = \frac{c_{ML}^*}{c_M^*} \quad (4)$$

It is well-known that for polyelectrolytes K' varies with the charge density (ϱ) on the polyionic complex. For very low metal-to-ligand ratios ϱ is connected with the degree of dissociation α_d of the polyacid. Since PAA has a fairly small intrinsic protolytic dissociation constant of $10^{-4.7} \text{ mol l}^{-1}$, α_d is practically equal to the degree of neutralization α_n unless this parameter is so small that the proton concentration is not negligible with respect to the carboxylate concentration. Our experiments are carried out for some pre-determined and not too low value of α_n , so that the concentration of carboxylate ligands is well-defined.

For a labile metal complex system, the pre-electrolysis current (I_e) can be formally written as a postulated function of the mean diffusion coefficient (\bar{D}) and the total metal concentration:

$$I_e \propto \bar{D}^p \cdot c_T^* \quad (5)$$

with

$$\bar{D} = (c_M^*/c_T^*) D_M + (c_{ML}^*/c_T^*) D_{ML} \quad (6)$$

The power p is related to the nature of the mass transport during the pre-electrolysis step. For example, it is $1/2$ for semi-infinite linear diffusion and $2/3$ for laminar convective diffusion⁵. However, in stripping voltammetric experiments, especially in case of a hanging mercury drop electrode, the hydrodynamic conditions are rather poorly defined. Then the validity of Eq. (5) or, for that matter, the value of p is uncertain. Eq. (6) is valid if the local ratios c_M/c_T and c_{ML}/c_T are independent from the distance to the electrode surface and this is only true in the case of a ligand excess such that c_L is invariant (and equal to c_L^*). The concentration of metal in the mercury drop, which is linearly proportional to the reoxidation peak current (I), will be proportional to the pre-electrolysis current and time (t_e):

$$I_e t_e \propto c_M(\text{Hg}) \propto I \quad (7)$$

Let us define Φ as the ratio of the reoxidation peak current for the complex system and the reoxidation peak current under conditions of no complexation. Combination of the equations (2), (5), (6) and (7) then gives:

$$\Phi = \left(\frac{\bar{D}}{D_M} \right)^p = \left(\frac{1 + \varepsilon K c_L^*}{1 + K c_L^*} \right)^p \quad (8)$$

with $\varepsilon = D_{ML}/D_M$.

For the arbitrary set of values $K = 5 \cdot 10^5$ and $p = 1/2$, Eq. (8) yields dependences of Φ on the concentration of deprotonated ligands (c_L^*) as presented in Fig. 1. Due to increase of K' , Φ will decrease with increasing ligand concentration. Three regions can be distinguished with different information content with respect to the different parameters in Eq. (8). Region A is most sensitive to the complex stability (K) (for mathematical details see Appendix A). The shape of the curve in region B is most sensitive to the value of p . The diffusion coefficient ratio ε has its main influence in region C, the tail of the complexation curve. From Eq. (8) it is immediately clear that for $Kc_L^* \gg 1$, Φ approaches the limit ε^p .

$$\Phi(c_L^*) = \lim_{c_L^* \rightarrow \infty} \left(\frac{1 + \varepsilon K c_L^*}{1 + K c_L^*} \right)^p = \varepsilon^p \quad (9)$$

In the case of macromolecular complexes with very low diffusion coefficients, D_{ML}/D_M may become so small that in region A the first term in \bar{D} (see Eq. (6)) is strongly dominant.

EXPERIMENTAL

Materials

The polyacrylic acid (PAA) solutions, with average molar masses of 50,000, 150,000 and 500,000 g mol^{-1} , were obtained from Polysciences, and used without further pretreatment. Stock solutions of c. 0.1 mol l^{-1} (in monomers) were prepared by dilution with water. Concentrations of carboxylic groups were determined by conductometric titration with potassium hydroxide. Stock solutions were stored in the dark at 4°C . Titrisol potassium hydroxide solutions (Merck), zinc(II) nitrate and potassium nitrate (both Baker) were of analytical-reagent grade. All solutions were prepared using demineralized tap water, produced by a Millipore Super-Q reverse osmosis system.

Apparatus

The Differential Pulse Anodic Stripping Voltammograms (DPASV) 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 was Ag/AgCl/KCl(sat.). The pulse duration was 40 ms and the pulse height was 25 mV. The deposition potential was -1.200 mV . The pre-electrolysis time and the rest period observed were 1 and 0.5 min, respectively. The scan rate in the stripping step was 5 mV s^{-1} . Purified nitrogen was used for deaeration and blanketing of the sample solutions. The experiments were carried out at 20°C .

Titration Procedure

Solutions of PAA were partially neutralized to a certain degree of neutralization α_n by adding the required amount of KOH. Aliquots of these solution were pipeted into the metal ion solutions, and DPASV voltammograms were recorded after each addition. Peak currents were corrected

for dilution due to addition of polyelectrolyte solution, so that they all refer to the same total metal concentration. KNO_3 was applied as supporting electrolyte at a concentration of 0.02 mol l^{-1} .

Fitting Procedure

In order to fit the experimental results to theoretical predictions from Eq. (8), a FORTRAN program was developed. A basic element of the program is the subroutine ZXMIN, taken from the IMSL library⁶.

RESULTS AND DISCUSSION

In Fig. 2, the experimental complexation curves for the Zn/PAA system with a molar mass of $50,000 \text{ g mol}^{-1}$ are plotted for two different degrees of neutralization. For $\alpha_n = 0.8$, using $p = 2/3$ and $\varepsilon = 0.077$ (as estimated from the high- c_L^* limit), the fitting procedure gives a $\log K$ value of 5.72 and a favourable correlation coefficient $r^2 (=0.989)$. According to Eq. (9), the use of $p = 1/2$ results in using a smaller value for ε in the fitting procedure. Thus using $p = 1/2$ and $\varepsilon = 0.032$ for the Zn/PAA system at $\alpha_n = 0.8$, the $\log K$ value is found to be 5.92 ($r^2 = 0.993$). The fit with $p = 1/2$ is somewhat better than for $2/3$. This finding seems to be in line with the results by Esteban et. al.⁴ who obtained values in the range 0.52–0.59 for the labile Zn/PMA system. In analyzing data of the reduction currents of some metals as function of their diffusion coefficients⁷, satisfactory fits are found with $r^2 = 0.984$ and $r^2 = 0.985$ for $p = 1/2$ and $p = 2/3$, respectively. It should be realized that the

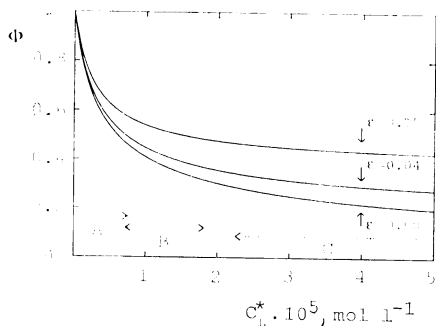


FIG. 1

Sensitivity of the Φ, c_L^* complexation curve to the different parameters. $K = 5 \cdot 10^5$, $p = 0.5$; values of ε are indicated. Further explanation in the text

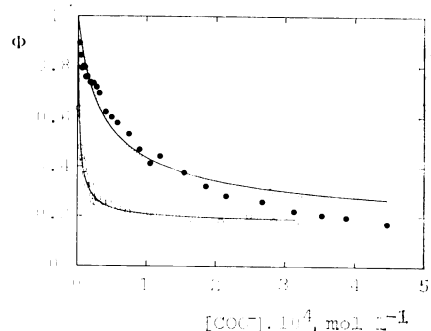


FIG. 2

Experimental and calculated values of Φ as a function of the carboxylate concentration for the Zn/PAA system with a molar mass of $50,000 \text{ g mol}^{-1}$ at $\alpha_n = 0.4$ (●) and 0.8 (○). Fit: $p = 1/2$ solid line; $p = 2/3$ dotted line

stability constant K is the most important parameter for speciation calculations, and that therefore very precise knowledge about the value of p is not a prerequisite. This point is of practical importance since in stripping voltammetric analysis p depends on the experimental arrangements and varies from one situation to another. For the present particular complexation curve, the qualities of the fits for $p = 1/2$ and $p = 2/3$ are hardly different and therefore the value of $\log K$ resulting from our experiments can be given as 5.8 ± 0.1 .

The complexation curves show that for $\alpha_n = 0.8$, Φ decreases much stronger with c_L^* than for $\alpha_n = 0.4$. This is due to the appreciably higher value of the stability K and in accordance with the general polyelectrolytic feature that counterion binding is stronger with higher polyionic charge density. Using the same sets of values for p and ε as above, $\log K$ values for $\alpha_n = 0.4$ are found to be 4.71 ($r^2 = 0.956$) and 4.55 ($r^2 = 0.959$) for $p = 1/2$, $\varepsilon = 0.032$ and $p = 2/3$, $\varepsilon = 0.077$, respectively. From Fig. 2 it can be seen that the level of the "tail" is somewhat higher for the calculated curve than for the experimental data. By using smaller values for ε the "tail" of the calculated curve may be expected to decrease. Still the effect of a lower ε on the quality of the fit is hardly significant: for $p = 1/2$, $\varepsilon = 0.01$ and $p = 2/3$, $\varepsilon = 0.02$, $\log K$ values were found to be 4.67 ($r^2 = 0.968$) and 4.45 ($r^2 = 0.968$), respectively. These findings are readily understood if one takes into account that the binding is quite weak and the influence of ε is yet small (compare Fig. 1). In accordance with this, the computed $\log K$ values are almost independent of the chosen ε and they may therefore be considered as reliable data.

In Fig. 3, the experimental values of Φ are plotted as a function of the PAA concentration for three Zn/PAA systems with different molar masses of the polyacid and a constant α_n of 0.8. Under these conditions the macromolecular ion is certainly in its expanded conformation due to the high charge. For the three different molar masses, the initial parts of the curves are practically the same, which indicates that the complex stabilities are identical (see Table I). All stability constants could be satisfactorily calculated after estimating ε from the tail of the complexation curve using either $p = 1/2$ or $p = 2/3$ according to Eq. (9). In Table I the stability constants obtained by the fitting procedure are collected for the three different molar mass values. Invariably, the quality of the fit is acceptable (that is, comparable to or within the experimental error). The differences between the correlation coefficients obtained by using $p = 1/2$ and $p = 2/3$, respectively, are not significant. This is the more general picture (for which the analysis of one separate curve, like Fig. 2, is not representative). It would seem tempting to give preference to the set of results obtained for $p = 1/2$ because it yields a remarkably constant K (variation 0.01). However, considering all other data⁴ and the uncertainties concerning p and ε , this is not very well justified. The conclusion that has to be drawn here is that both sets deserve their credit and that under the given conditions K is approximately $10^{5.8}$ and definitely independent of the molar mass of the polyacid. Thus the strength

of the binding of Zn(II) to the carboxylate group of PAA is not affected by the molar mass of the polyacid.

The results are the more elegant since, unlike the resulting K value, the *shape* of the complexation curve is clearly affected by the molar mass of the polyion. With increasing molar mass, Φ decreases to a lower level, in accordance with a decrease of the diffusion coefficient of the complex with increasing molar mass.

Just for illustration, the fractions of free and bound metal have been calculated on the basis of Eq. (2) for the three different molar masses. Figure 4 shows the results

TABLE I
Stability constants K for the Zn/PAA system as a function of the molar mass of the polyacid at $\alpha_n = 0.8$

Molar mass	p	ε	$\log K$	r^2
50,000	1/2	0.032	5.92	0.993
	2/3	0.077	5.72	0.989
150,000	1/2	0.006	5.92	0.990
	2/3	0.023	5.68	0.994
500,000	1/2	0.002	5.91	0.938
	2/3	0.008	5.65	0.968

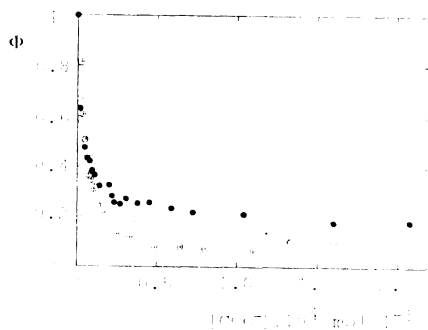


FIG. 3
Experimental values of Φ as a function of the carboxylate concentration for the Zn/PAA system with different molar masses at $\alpha_n = 0.8$: ● 50,000; ○ 150,000; ⊕ 500,000

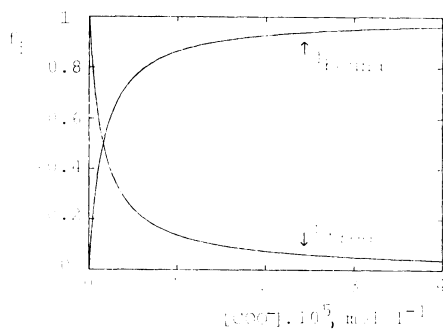


FIG. 4
Fractions of free and bound Zn(II) as a function of the carboxylate concentration for the Zn/PAA system with arbitrary molar mass at $\alpha_n = 0.8$. ($\log K = 5.8$)

for the Zn/PAA system for $\log K = 5.8$ at $\alpha_n = 0.8$. As conclusively proven, this distribution holds for any molar mass of the polyelectrolytic ligand.

APPENDIX

The sensitivity region of Φ with respect to K can be found after taking the derivative of Eq. (8)

$$\frac{d\Phi}{dK} = \frac{p(1 + \varepsilon K c_L^*)^{p-1} c_L^*(\varepsilon - 1)}{(1 + K c_L^*)^{p+1}} \quad (A1)$$

The independent variable in a complexation experiment is the ligand concentration c_L^* . The value of c_L^* where the sensitivity of Φ to K has a maximum, can be found by solving

$$d(d\Phi/dK)/dc_L^* = 0 \quad (A2)$$

and gives:

$$\varepsilon K^2 c_L^{*2} + pK(1 + \varepsilon) c_L^* - 1 = 0. \quad (A3)$$

For small values of ε ($\varepsilon \rightarrow 0$) Eq. (A3) approaches

$$pKc_L^* = 1. \quad (A4)$$

From Eq. (A4) it can be easily seen that Φ is most sensitive to K if Kc_L^* is in order of 1.5 to 2 for $p = 2/3$ and $p = 1/2$, respectively. For much smaller or much higher values of Kc_L^* , Φ will be too close to unity or too small for reliable computation of K .

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