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Influence of the counterion concentration on the formation constants of some metal/polycarboxylate complexes: Study by differential pulse anodic stripping voltammetry

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Abstract

The influence of counterion concentration on the complex formation of Zn(II), Cd(II) and Pb(II) with polymethacrylic acid (PMA) and polyacrylic acid (PAA) is studied by differential pulse anodic stripping voltammetry (DPASV). Titrations of Zn(II) or Cd(II) or Pb(II) with partially neutralized PMA or PAA at different KNO_3 concentrations (C_K) allows the precise determination of the apparent formation constant (K) of the systems, through analysis of current data alone and both current and potential data obtained by DPASV. Linear relationship between log K and log C_K, with slope values within the range -1.7 to -2.2, are obtained. The possible causes of some anomalous behaviours observed for PAA systems with respect to the voltammetric model assumed are discussed.

Keywords: Voltammetry; Competitive counterion binding; Heavy metal; Polycarboxylic acid

1. Introduction

Electrochemical methods, especially voltammetry, are popular in metal speciation studies because, in principle, they may be used to determine the distribution of some metal ions among the "free" and the "complexed" forms [1,2]. The applicability of voltammetry to speciation in rather involved systems such as polyelectrolytic systems is relatively recent [3]. The voltammetric approach to the basic scheme of the reduction of an electroactive metal-ion M in the presence of an excess of a macromolecular ligand L, which may associate to give the labile electroinactive complex ML, has received rigorous treatment for any set of rate constants and diffusion coefficients, allowing an exact solution in the Laplace domain [4]. For the labile case, a solution in the real domain is available. The validity of this approach was confirmed for labile systems, e.g. Zn–polycarboxylic acids, by different polarographic techniques, such as sampled direct current (DCP), normal pulse (NPP) and reverse pulse (RPP) polarography [5].

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The voltammetric theory for a basic scheme as above-mentioned is not yet available for relevant analytical techniques such as differential pulse polarography (DPP) and anodic stripping voltammetry (ASV). In the case of ASV, the complexity of the hydrodynamic conditions during the pre-electrolysis step has prevented the theoretical resolution of the problem up to now. In a first approach, the application of the above model to ASV data, obtained from labile systems, has been carried out by postulating [6] the validity of a modified equation analogous to that rigorously deduced [3,4] but including a parameter p related to the nature of the mass transport during the pre-electrolysis step (convective diffusion conditions); p may be expected to lie between $\frac{1}{2}$ (semi-infinite linear diffusion) and $\frac{2}{3}$ (laminar convective diffusion) [6]. The equations to be considered for ASV peak currents (I_p) and peak potentials (E_p) are:

$$\phi = \frac{I_p\,(\text{with L})}{I_p\,(\text{without L})} = \left(\frac{\bar{D}}{D_M}\right)^p = \left(\frac{1+\epsilon K C_L^*}{1+K C_L^*}\right)^p \qquad (1)$$

$$F = \exp\left[-\frac{n\mathcal{F}}{RT}\,\Delta E_p - \ln\phi\right] = 1 + K C_L^* \qquad (2)$$

where ϕ is the normalized current, C_i^* and D_i are the bulk concentration and the diffusion coefficient of species i, respectively, $\epsilon = D_{ML}/D_M$, K is the formation constant of the complex ($K = C_{ML}^*/C_M^* C_L^*$), ΔE_p is the potential shift due to complexation, F is a function defined similarly to the Leden Function of zero order and $\bar{D}$ is the mean diffusion coefficient of the complex system:

$$\bar{D} = \frac{C_M^*}{C_T^*} D_M + \frac{C_{ML}^*}{C_T^*} D_{ML} \qquad (3)$$

where C_T^* is the total metal-ion concentration (free plus bound).

This semi-empirical approach allowed satisfactory interpretation of experimental results for a number of labile systems, e.g. Zn, Cd/polycarboxylic acids [6,7] and Cd/polysaccharides [8]. This is especially interesting because differential pulse anodic stripping voltammetry (DPASV) allows extremely low metal-to-ligand ratios to be achieved, and at concentration levels as low as those occurring in natural aquatic media.

Several classes of natural macromolecular ligands (humic and fulvic acids, for instance) contain a variety of metal-binding groups and, as a consequence, their complexes with metal ions exhibit not only polyelectrolytic but also polyfunctional effects, thus introducing additional difficulties in the interpretation of experimental results. Homofunctional polycarboxylic acids, such as polyacrylic acid (PAA) or polymethacrylic acid (PMA) with a fairly sharp molecular-mass distribution range, have been widely used as model ligands in methodological studies concerning to macromolecular ligands.

In the present paper, the complex formation of Zn(II), Cd(II) and Pb(II) by the model polyelectrolytes PAA and PMA is studied, by means of DPASV, in the light of the approach described above. The main subject is to determine the influence of the concentration of the counterion used in the supporting electrolyte on the values of the formation constants of the complexes formed in these systems.

In order to determine accurately the dependence of K on the supporting electrolyte concentration, C_K, a C_K range as wide as possible must be used. This means for each system the use of different values of the degree of neutralization, α_n, adjusted according to the different magnitudes of the formation constant of the complexes (Pb > Cd > Zn), as well as the use of different conditions to obtain ϕ vs. C_L^* and F vs. C_L^* plots most similar to those expected theoretically (eqs. 1 and 2). Although complexation parameters (mainly K) are likely to depend on α_n, the results obtained (see section 3) seem to indicate the relationship of K to ionic strength is α_n-independent, at least under the experimental conditions used.

Although experimental data on these systems are already available from pulse polarography [5,7,9–12] or stripping voltammetry [6,7,13,14], systematic voltammetric studies about the influence of the counterion concentration on the bivalent metal ion/polyion binding strength are still required. They are still scarce in comparison with conductometric studies [15] and there is a lack of general agreement on the data reported. Discrepancies are found, for instance, between the results obtained by voltammetric and conductometric means for the Zn/PMA [13] and Zn/PAA [16] systems and those reported in a previously described pulse polarographic study of the Cd, Pb/PAA, PMA (partially esterified) systems [11,12] or those obtained similarly for polysaccharides [7] and DNA [17].

2. Experimental

2.1 Reagents and apparatus

Polyacrylic acid (PAA) and polymethacrylic acid (PMA) solutions obtained from BDH laboratory reagent grade (average molecular masses, according to BDH, 230,000 and 26,000 g mol^{-1}, respectively), were used to prepare stock solutions in water of ca. 0.1 mol L^{-1} (in monomers). The total number of carboxylic groups was determined by conductometric acid-base titration. The intrinsic dissociation constants of PAA and PMA appeared to be $10^{-4.7}$ and $10^{-4.9}$, in mol L^{-1} units, respectively [11]. The diffusion coefficients of PAA and PMA, as calculated from literature data [9], are approximately 10^{-7} and 1.5 10^{-7} cm^2 s^{-1}, respectively.

All other reagents used were analytical grade. Carbonate-free KOH was used for the partial neutralization of the polyacid solutions. As supporting inert electrolyte KNO_3 was applied. Solutions of $Zn(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ were used at the concentration level of 10^{-6} mol L^{-1}. Ultrapure water (Culligan water purification system) with a conductivity (after degassing traces of CO_2) lower than 0.5 μS cm^{-1} was used in all experiments.

In the voltammetric titrations of Zn(II), Cd(II) and Pb(II) with PAA and PMA, the differential pulse anodic stripping voltammograms were obtained with a 646 VA Processor/663 VA Stand Metrohm, attached to a Dosimat 665 Metrohm for the automatic addition of the titrant solutions. In the voltammetric titration of the Zn/PMA system with KNO_3, and in order to work at KNO_3 concentration levels below 0.003 mol L^{-1} (inaccessible to the 646 VA Processor), an Autolab system (Ecochemie) attached to a 663 VA Stand (Metrohm) and to a personal computer, by means of the electrochemical software package GPES2, was used. The working electrode, the reference electrode, to which all potentials are referred, and the counterelectrode were an HMDE (Hanging Mercury Drop Electrode), a Ag/AgCl,KCl(sat.) and a glassy carbon electrode, respectively. Pulse durations of 40 ms, pulse heights of 50 mV, deposition potentials of −600 mV for Pb^{2+}, −800 mV for Cd^{2+} and −1200 mV for Zn^{2+} were used. The pre-electrolysis time and the rest period used were 1 and 0.5 min, respectively. The scan rate in the stripping step was 10 mV s^{-1}. Measurements were taken at 25° ± 0.5°C. Purified nitrogen was used for deaeration and blanketing of the sample solutions.

Acid-base conductometric titration of PMA and PAA stock solutions were performed with an Orion cell ($k = 1.03$ cm^{-1}) attached to an Orion 120 Microprocessor Conductivity Meter. pH measurements were effected with an Orion SA 720 pH-meter.

2.2 Procedures

2.2.1 Voltammetric titration of Zn(II), Cd(II) and Pb(II) with PAA and PMA

Potassium nitrate-containing solutions of PAA and PMA were partially neutralized with KOH up to a certain degree of neutralization α_n. Aliquots of these solutions were automatically added to the metal ion solutions (also containing KNO_3, at the same concentration as the ligand solution), and the voltammograms were recorded after each addition. Experiments were continued until large excesses of ligand over metal were reached. In this way, the ratio C_L^*/C_T^* was usually increased from zero (the blank solution) to > 200. It must be noticed that after the first addition of L, $C_L^*/C_T^* = 6$–15 (depending on the particular system), and the condition $C_L^* \gg C_T^*$ was still not fulfilled at all. This condition was quickly achieved after some further additions of L.

Peak currents were corrected for dilution effects in order to refer them to a constant total metal ion concentration.

In order to fit the experimental ϕ values to the theoretical predictions (eq. 1), the non-linear regression data analysis program ENZFITTER [18] was used. From the standard deviations calculated by the program, and by using the usual statistical treatment with Student's t test at the 95% confidence level, the confidence ranges of each fitted K value were calculated. Fixed values for p ($p=\frac{1}{2}$) and ϵ (0.019 and 0.023 for PAA- and PMA-systems, respectively [9–12]) were adopted. Leyte and Mandel [19] have found, by potentiometric titrations, evidence of a transition between two conformations for PMA. This transition strongly depends on the degree of neutralization, but no significant dependence on ionic strength was found. Similarly, the proportion of PAA present in the two different molecular conformations was independent of the ionic strength, depending only on the degree of dissociation at constant temperature [20]. As a consequence, fixed values of ϵ (from $D_L \approx D_{ML}$) can be assumed. The assumption $p=\frac{2}{3}$ does not affect the results significantly.

In the fitting of F (eq. 2), simple linear regression analysis was used.

2.2.2 Voltammetric titration of a Zn/PMA solution with KNO_3

Aliquots of 0.1 and 1 mol L^{-1} KNO_3 solutions were manually added to 25 ml of a solution containing 10^{-6} mol L^{-1} of Zn(II) and 10^{-4} mol L^{-1} of PMA partially neutralized with KOH to an α_n value of 0.8 ($C_L^* = 8\ 10^{-5}$ mol L^{-1}), and the voltammograms were recorded after each addition. The same KNO_3 additions were performed to 25 ml of a solution containing only 10^{-6} mol L^{-1} of Zn(II), and the voltammograms were also recorded in order to obtain a Zn(II) blank (peak intensity and potential in the absence of ligand) for each KNO_3 concentration.

3. Results and discussion

The influence of the counterion (K^+) concentration (C_K) on both Zn(II) systems was studied within the range 0.004–0.2 mol L^{-1} in KNO_3 for a 10^{-6} mol L^{-1} Zn(II) concentration in the presence of PAA at $\alpha_n = 0.7$ or PMA at $\alpha_n = 0.8$. The experimental ϕ vs. C_L^* plots of the Zn/PMA system are shown in Fig. 1. Similar plots are obtained for the Zn/PAA system. Moreover, linear plots of F vs. C_L^*, with increasing slope values when C_K decreases, are obtained for both Zn(II) systems. All these results agree with those theoretically expected according to the model used [4], especially at low C_K values, owing to the increasing stability of Zn(II)-polycarboxylate complexes at decreasing counterion concentrations.

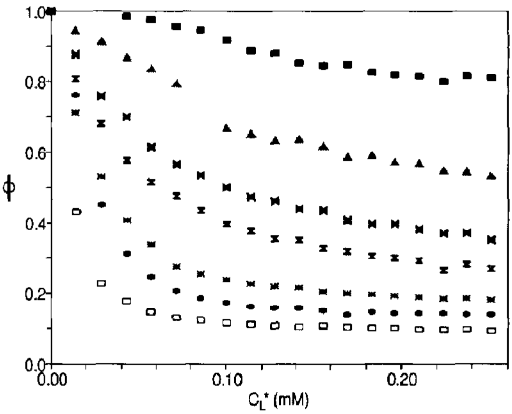

Fig. 1. Zn/PMA system: normalized peak current (ϕ) values as functions of polycarboxylate concentration at different counterion (K^+) concentrations. (□) 0.004, (+) 0.01, (∗) 0.02, (⌧) 0.04, (×) 0.06, (▲) 0.1, and (■) 0.2 mol L^{-1} KNO_3. Zn(II)-ion concentration 10^{-6} mol L^{-1}, and $\alpha_n = 0.7$.

For the Cd(II) systems, the influence of C_K was studied in the range 0.004–0.20 mol L^{-1} in KNO_3 for 10^{-6} mol L^{-1} Cd(II) in the presence of PMA or PAA at $\alpha_n = 0.6$.

For Cd/PMA, plots of ϕ vs. C_L^* (Fig. 2) and linear relationships of F vs. C_L^* were similar to those theoretically expected. The study of the plots ϕ vs. C_L^* at seven different Cd(II) concentrations (in the range 5 10^{-8}–4 10^{-6} mol L^{-1}), and the ANOVA (95% confidence level) of the constants evaluated therefrom, show the independence of the results on the Cd(II) concentration, similarly to what was previously observed for Zn(II) systems [7]. At $C_K \leq 0.01$ mol L^{-1} very sharp decreases of ϕ at low C_L^* values were

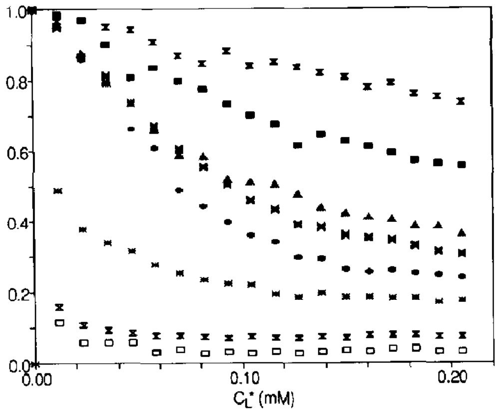

Fig. 2. Cd/PMA system: normalized peak current (ϕ) values as functions of polycarboxylate concentration at different counterion (K^+) concentrations. (□) 0.004, (⧗) 0.01, (∗) 0.02, (+) 0.03, (×) 0.04, (▲) 0.06, (■) 0.1, and (⧗) 0.15 mol L^{-1} KNO_3. Cd(II)-ion concentration 10^{-6} mol L^{-1} and $\alpha_n = 0.6$.

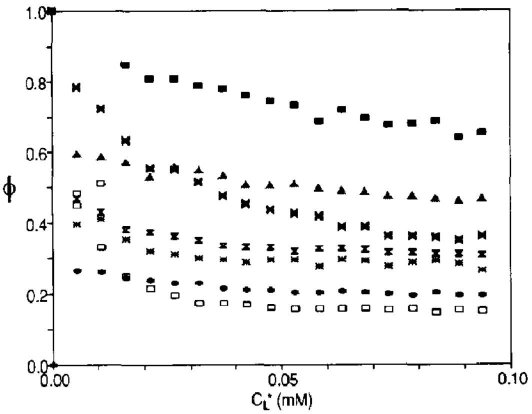

Fig. 4. Pb/PMA system: normalized peak current (ϕ) values as functions of polycarboxylate concentration at different counterion (K^+) concentrations. (□) 0.01, (+) 0.02, (∗) 0.04, (⧗) 0.06, (×) 0.1, (▲) 0.15, (■) 0.25 mol L^{-1} KNO_3) Pb(II)-ion concentration 10^{-6} mol L^{-1}, and $\alpha_n = 0.3$.

observed. At $C_K = 0.01$ mol L^{-1}, ϕ values reached were similar to those predicted by eqn. (1), while at $C_K = 0.004$ mol L^{-1} those ϕ values were lower than those predicted.

For Cd/PAA, at $C_K \le 0.08$ mol L^{-1} approximate normal shaped ϕ vs. C_L^* plots are obtained (Fig. 3), although with very steep decreases of ϕ at low C_L^* values. At $C_K > 0.08$ mol L^{-1} the curves show a progressive deformation, particularly apparent at the lowest C_L^* values. At $C_K < 0.04$ mol L^{-1}, the F vs. C_L^* plots are clearly formed by a linear part, at low C_L^* values, followed by an F-constant part, at higher C_L^* values. At $C_K \ge 0.04$ mol L^{-1} the linear region shades off into the horizontal region, it being more difficult for the two regions to be distinguished as C_K increases.

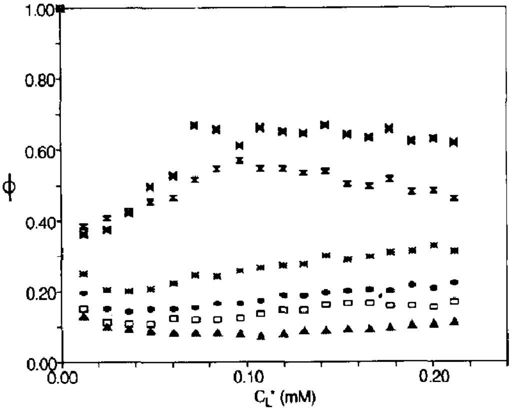

Fig. 3. Cd/PAA system: normalized peak current (ϕ) values as functions of polycarboxylate concentration at different counterion (K^+) concentrations. (▲) 0.04, (□) 0.06, (+) 0.08, (∗) 0.1, (⧗) 0.15 and (×) 0.2 mol L^{-1} KNO_3. Cd(II)-ion concentration 10^{-6} mol L^{-1}, and $\alpha_n = 0.6$.

For the Pb(II) systems, the influence of C_K was studied within the range 0.01–0.25 mol L^{-1} in KNO_3 for a 10^{-6} mol L^{-1} Pb(II) in the presence of PMA or PAA at $\alpha_n = 0.3$. Plots of ϕ vs. C_L^* for Pb/PMA are shown in Fig. 4. For Pb/PAA, plots of ϕ vs. C_L^* are very similar to those shown for Cd/PAA (Fig. 3), with a progressive deformation of the curves at $C_K > 0.06$ mol L^{-1}, more apparent at the lowest C_L^* values. For both Pb(II) systems, similarly to the Cd/PAA system, most of the F vs. C_L^* plots show a linear part followed by an F-constant one.

The presence of minima in some ϕ vs. C_L^* curves was only observed for Cd/PAA and Pb/PAA systems at $C_K \ge 0.1$ mol L^{-1}. This is not surprising after previous investigations [6], but their causes are still unknown. These could be related to adsorption effects, but, under the experimental conditions used, losses of Cd(II) or Pb(II) by adsorption onto the cell materials begin to be significant at pH > 6.5 or pH > 4, respectively, in agreement with previous data [21–23]. Losses of Cd(II) must be negligible along the titrations of Cd(II) with PAA, because $pH < 6.5$ in all cases. Then, the anomalous behaviour for the Cd/PAA system at $C_K \geq 0.1$ mol L^{-1} cannot be attributed to this cause. Nonetheless, for the Pb/PAA system at $C_K \geq 0.1$ mol L^{-1} such a forceful assumption neglecting adsorption onto cell material cannot be made because along the titration $pH > 4$. However, adsorption should be not very important because of: (i) the global behaviour of the systems at the different C_K values is not very different from that theoretically expected and from that of the other systems; (ii) the adsorption should be more important at low C_K values than at high C_K values, due to the competition between K^+ and Pb^{2+} for the adsorption sites.

On the other hand, the very sharp decreases of ϕ at low C_L^* values for Cd(II) systems at $C_K \leq 0.01$ mol L^{-1} cannot be easily justified. In a pulse polarographic study of some metal ion/polycarboxylates, it was noticed [11] that at $C_K < 0.01$ mol L^{-1} (with $[M^{2+}] = 10^{-4}$ mol L^{-1}) migrational mass transport of M^{2+} species may be non-negligible, and increased currents appear. In the present case, however, the presence of migrational mass transport seems negligible because from a 4000 to 10,000-fold excess of supporting electrolyte is present. Furthermore, it was supported recently [13] that by ASV complete complexation curves can be accurately obtained for very low metal ion levels. Thus, under conditions of a 10- to 100-fold excess of ligand over metal ion and a 10- to 100-fold excess of supporting electrolyte over ligand, it was possible to study the M^{2+}/PMA, PAA interactions over an ionic strength range of some four orders of magnitude (i.e., from 10^{-4} to 1 mol L^{-1} for M^{2+} 10^{-7} mol L^{-1}, or less), which reaches even lower C_K values than those used in the present work.

Table 1 summarizes the log K values obtained from ϕ vs. C_L^* and F vs. C_L^* data at different C_K values, for such cases where the behaviour agrees reasonably with that predicted from the model. For Pb/PMA, log K obtained from the simultaneous fit of p, ϵ and K are also indicated. For the Cd/PAA, log K values have been determined only from the linear F vs. C_L^* plots at low

Table 1

Formation constants of the metal/polycarboxylate complexes studied at different KNO_3 concentrations (C_K). log $K(\phi)$ and log $K(F)$ are the values obtained from ϕ vs. C_L^* and F vs. C_L^*, respectively.

System	α_n	C_K (M)	log $K(\phi)$	log $K(F)$
Zn/PAA	0.7	0.004		6.78(±0.03)
		0.01		6.32(±0.02)
		0.02	6.2 (±0.3)	5.67(±0.01)
		0.04	5.36(±0.01)	5.11(±0.02)
		0.06	4.97(±0.01)	4.75(±0.02)
		0.1	4.45(±0.02)	4.27(±0.02)
		0.2	4.1 (±0.1)	3.66(±0.07)
Cd/PAA [a]	0.6	0.01		7.81(±0.03)
		0.02		7.20(±0.04)
		0.03		6.91(±0.02)
		0.04		6.59(±0.03)
		0.06		6.21(±0.07)
		0.08		5.97(±0.07)
		0.1		5.6 (±0.1)
Pb/PAA	0.3	0.01	6.7 (±0.3)	
		0.02	6.16(±0.01)	
		0.04	5.6 (±0.1)	
		0.06	5.2 (±0.1)	
		0.1	4.75(±0.03)	
Zn/PMA	0.8	0.004		6.45(±0.03)
		0.01	5.7 (±0.2)	5.70(±0.04)
		0.02	5.3 (±0.1)	5.19(±0.03)
		0.04	4.77(±0.04)	4.65(±0.03)
		0.06	4.51(±0.02)	4.39(±0.02)
		0.1	4.04(±0.03)	3.84(±0.03)
		0.2	3.37(±0.04)	3.42(±0.04)
Cd/PMA	0.6	0.02	5.49(±0.05)	5.22(±0.02)
		0.03	4.7 (±0.1)	4.81(±0.05)
		0.04	4.5 (±0.1)	4.57(±0.04)
		0.06	4.42(±0.06)	4.35(±0.02)
		0.1	4.00(±0.04)	3.99(±0.03)
		0.15	3.57(±0.03)	3.72(±0.03)
Pb/PMA	0.3	0.01	6.3 (±0.1)	
		0.02	6.05(±0.01)	
		0.04	5.6 (±0.1)	
		0.06	5.4 (±0.1)	
		0.1	5.00(±0.01)	
		0.15	4.8 (±0.1)	
Pb/PMA [b]	0.3	0.02	6.54(±0.01)	
		0.04	6.37(±0.02)	
		0.06	6.0 (±0.3)	
		0.1	5.05(±0.01)	

[a] System Cd/PAA: Values obtained from the initial linear segment of F vs. C_L^*.

[b] System Pb/PMA: Simultaneous fit of p, ϵ and K in ϕ vs. C_L^* plots. The mean fitted values of p and ϵ are $p = 0.4$ and $\epsilon = 0.01$.

C_L^* values. It can be observed in this case that the evaluated confidence ranges of log K increase with increasing C_K values, because of the above-mentioned uncertainty on the F vs. C_L^* dependences. Table 2 summarizes the slopes of the linear relationships between log K and log C_K, the mean slope values being usually around -2.0.

It should be noted that the data obtained in the study of the Zn/PMA system at $\alpha_n = 0.8$ could be affected by adsorption on the cell materials, especially at low C_K values. However, this does not seem to affect the relationship between log K and log C_K, which is very similar to those obtained in systems where adsorption is clearly absent. Furthermore, a complementary study of the Zn/PMA system at $\alpha_n = 0.8$ has been made by means of the titration of a Zn/PMA solution (ligand-to-metal ratio 80:1) with KNO_3 (where the adsorption conditions can be very different). Figure 5 summarizes the log K vs. log C_K dependences obtained from the two different experimental approaches. Although in this figure some differences in the absolute values obtained from different approaches are noticed, linear dependences of log K vs. log C_K are also reached in the second procedure, with mean slope values of ca. -1.9.

Table 2

Slope values of the linear relationships between the formation constant (log K) and the logarithm of the KNO_3 concentration, from the voltammetric titrations of metal-ions with polyacids.

System	α_n	Variable	Slope of log K vs. log C_K
Zn/PAA	0.7	ϕ	-2.2 (± 0.1)
		F	-1.9 (± 0.2)
Cd/PAA	0.6	F [a]	-2.0 (± 0.2)
Pb/PAA	0.3	ϕ	-2.01(± 0.04)
Zn/PMA	0.8	ϕ	-2.0 (± 0.3)
		F	-1.8 (± 0.1)
Cd/PMA	0.6	ϕ	-2.1 (± 0.4)
		F	-1.7 (± 0.2)
Pb/PMA	0.3	ϕ	-1.5 (± 0.1)
		ϕ [b]	-2.1 (± 0.3)

[a] Fitting of the initial points of the F vs. C_L^* plot.

[b] Results obtained in the simultaneous fit of K, p and ϵ inside the I range 0.02–0.10 mol L^{-1}. The mean fitted values of p and ϵ are $p = 0.4$ and $\epsilon = 0.01$.

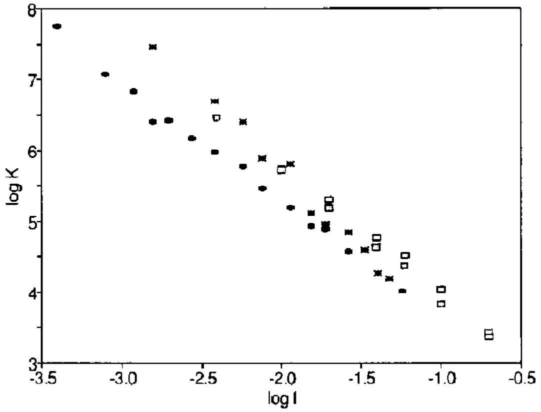

Fig. 5. Formation constant (K) values as functions of the total ionic strength (I) for the Zn–PMA complex at $\alpha_n = 0.8$, obtained from two series of experiments using different experimental approaches: (□,■) Values obtained from ϕ and F, respectively, through PMA titration of Zn(II) solutions (10^{-6} mol L^{-1} Zn(II); 0 to 2.5 10^{-4} mol L^{-1} polycarboxylate). (*,+): Values obtained from ϕ and F, respectively, through KNO_3 titration of a Zn(II)/PMA solution (10^{-6} mol L^{-1} Zn(II); 8 10^{-5} mol L^{-1} polycarboxylate).

From a qualitative point of view the influence of small ions on highly charged polyions is rather involved [24]. The presence of both univalent cations and univalent anions, which are usually present in the supporting electrolyte, affects the binding of bivalent metal ions by the polyion through several mechanisms, the substitution and the screening effects being the most significant. The first effect is related to the binding of M^+ by the polyion and the further competition between M^{2+} and M^+, involving the M^+/M^{2+} exchange. The second effect is related to the accumulation of free M^+ in the diffuse layer around the polyelectrolyte, controlling the effective charge density of the polyion, which also affects the M^+/M^{2+} exchange. As a consequence, the decrease in the log K values when the counterion concentration increases can be justified, more than by activity effects (lowering of activity coefficients), by the competition between M^{2+} and M^+, the competition being progressively less favorable for the M^{2+}-ions.

Complexation of M^{2+} displaces a certain number of M^+-ions initially bound to the polyion, but the stoichiometry of the process is still under discussion. Van Leeuwen [13] points out that, as long as $[K^+] \gg [L] \gg [M^{2+}]$ (which is true for most of the data presented, especially after some additions of PMA or PAA during the titrations), the thermodynamic equilibrium constant K_{th} for this exchange reaction is related to the apparent stability constant (K) by:

$$K = \frac{C^*_{ML}}{C^*_M C^*_L} \approx \frac{[MK_{s-\nu}L]}{[M^{2+}][K_sL]} = K_{th}\frac{1}{[K^+]^{\nu}} \qquad (4)$$

ν being the exchange ratio between K^+ and M^{2+}.

Equation (4) shows that log K and log C_K are indeed linearly related, and that the slope value of the linear relationship yields the exchange ratio (ν). The exchange ratios calculated from the present data (Table 2), obtained at relatively high α_n values (especially for Cd(II) and Zn(II) systems), are also coherent with a tentative general conclusion drawn for several M^{2+}/PAA, PMA (partially esterified) systems [11] which points out that the slope of log K vs. log C_K can reach a limiting value of -2 at high enough α_n values and low enough C^*_L values. Furthermore, these results are similar, although slightly higher, than those obtained for the systems Cd/alginic acid/KNO_3, ranging from 1.4 to 1.8 [8], Cd/pectinic acid/KNO_3, ranging from 1.26 to 1.59 [8] and Cd/DNA/KNO_3, about 1.67 [17]. The results here reported agree qualitatively with those obtained, by conductometric and voltammetric means, for Zn/PMA/KNO_3 [13], although the slope values are surprisingly lower (between 0.9 and 1.15). It should be noticed that conditions used in Ref. [13] (10^{-7} mol L^{-1} Zn(II), and C_K ranging from 10^{-1} to 10^{-4} mol L^{-1}) are different from those used here (10^{-6} mol L^{-1} Zn(II), glass cell and C_K ranging from 0.2 to 4 10^{-3} mol L^{-1}).

The results here described are coherent with many findings observed with different biopolymers, although the ascription of these results to some particular model is unclear. Thus, for instance, Record et al. [25] have developed a general thermodynamic analysis, based on the polyelectrolyte theory of Manning [26], of univalent ion effects on the observed association constants of ligand–nucleic acid interactions. The model explains the linear relationships found in the log K vs. log C_K plots, and takes the slope of such a plot as a measure of the number of charge interactions, or ion pairs, formed between ligand and nucleic acid. For olygolysines with z charge in the range $3 \le z \le 8$ and for polyamines with $2 \le z \le 4$, the slope values were all in the range $-0.82z$ to $-0.95z$, centered on the value $-0.88z$ (-1.76 for divalent ions) [27].

However, there are other models (e.g., counterion condensation model by Manning [28] for the salt-free limit) that predict a value equal to z for the slope $-$dlog K/dlog C_{M^+}. That model holds, however, for more complicated systems (interactions of olygocations with DNA and with ionic bilayers).

4. Conclusions

Voltammetry can be a valuable tool in the analysis of metal/polyelectrolyte systems at low metal concentrations, especially after a rigorous theoretical approach is available [3,4]. However, voltammetric results for the zinc/polyacrylate and zinc/polymethacrylate systems show some discrepancies with those by conductometric means. Because different experimental conditions are used for the two techniques, additional studies with several model systems are required in order to clarify the nature of such apparent discrepancies.

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