POLAROGRAPHY AND STRIPPING VOLTAMMETRY OF LEAD–POLYCARBOXYLATE COMPLEXES ON DROPPING MERCURY AND ROTATING DISC ELECTRODES

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Abstract. The influence of counterion charge, concentration, and pH of the solution on the complex formation of Pb^{2+} with polymethacrylic acid (PMA) and polyacrylic acid (PAA) was studied by different polarographic techniques. Titration of a polarographically detectable metal such as Pb^{2+} with polyacids allows precise determination of the apparent formation (stability) constant K of the complex through analysis of current data. It is shown that calculated and graphically determined values of K are in good agreement for experiments on dropping mercury and rotating disc electrodes. Linear relationships between $\log K$ and $\log a$ (activity of the counterion) were obtained and slope values characterizing the exchange ratio in the complex between Pb^{2+} and counterion were -0.5 (K^+) and -1.2 (Ca^{2+}), respectively. Studies at different pH values within the range 3.5–7 showed increasing stability constant with increasing pH. Slopes of $\log K$ vs. pH plots determined using different polarographic techniques were 0.5 ± 0.05 for PAA–K^+, PMA–K^+, and PMA–Ca^{2+} and 0.65 ± 0.05 for PAA–Ca^{2+}.

Key words: voltammetry, complexing of heavy metals, polycarboxylic acids.
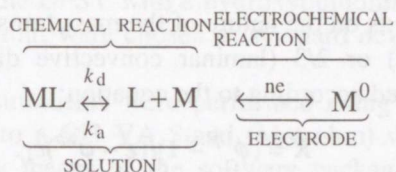
INTRODUCTION

Voltammetric techniques, especially stripping voltammetry, are most powerful tools in environmental analysis, because they allow direct speciation of heavy metals in natural waters at very low metal concentration levels. Speciation of natural systems deals with the complexation between metal ions and macromolecular ligands such as humic and fulvic acids, polysaccharides, proteins, etc. [1]. The interpretation of the voltammetric results in these systems presents difficulties due to the polyfunctional character of the macromolecular ligands, differences between diffusion coefficients of the complexes, adsorption effect on colloidal particles, etc. The colloidal fraction is thought to be a mixture of macromolecular complexes in the solution and dispersed microparticles. Studies

have shown that the dissolved and colloidal Pb show large intra- and interestuarine variations as well as significant seasonal variations in seawater [2, 3]. Although these results support the general conclusion that particulated metals reactivity follows the trend Cu < Cd << Pb, little is known about the physico-chemical interactions between dissolved and colloidal material.

Heavy metal complexes with natural ligands [1–4] show some similar behaviour with metal–synthetic polyacid complexes. Important groups of natural ligands such as humic acids and proteins are of a macromolecular nature and their complexes with metal ions exhibit some typical features. Amongst these features are polyelectrolytic effects, e.g. the variation of the stability constant with the effective charge of the macromolecular species, and the strongly reduced value of the diffusion coefficient of the complex as compared with the free metal ion. For complex formation properties of natural polyelectrolytes homofunctional synthetic polyacids such as polyacrylic acid (PAA) and polymethacrylic acid (PMA) are found to be satisfactory model compounds, which have been used in the interpretation of speciation studies of metal ions in natural waters [1].

The voltammetric approach to the basic scheme of the reduction of an electro-active metal ion M in the presence of an excess of a macromolecular ligand L, which may associate to give the labile electroinactive complex ML,

$$
\underbrace{ML \underset{k_a}{\overset{k_d}{\leftrightarrow}} L + M}_{\text{SOLUTION}} \quad \underbrace{\underset{}{\overset{ne}{\longleftrightarrow}} M^0}_{\text{ELECTRODE}}
$$

$$\underbrace{}_{\text{CHEMICAL REACTION}} \underbrace{}_{\text{ELECTROCHEMICAL REACTION}}$$

was developed in [5, 6]. In this scheme, M^0 denotes the metal atom and k_a and k_d are the association and dissociation rate constants, respectively. The ratio of the rate constants of the chemical reaction determines the stability constant K of the complex:

$$K = k_a/k_d = c_{ML}/c_M c_L, \tag{1}$$

where c_M, c_L, and c_{ML} are bulk equilibrium concentrations of free metal, free ligand, and ML complexes. The electrochemical reaction is assumed to be fast enough to render the system electrochemically reversible. The factors such as the diffusion coefficient of the complex D_{ML} and the dissociation kinetics of the complex prescribe the voltammetric response of the complex system. In the case of an electrochemically labile complex the chemical equilibrium between M and ML is maintained at all distances from the electrode. If the dropping mercury electrode is employed the overall lability criterion for a complexing system is given by [7]:

$$k_d \left(\frac{D_M}{k_a c_L} \right)^{1/2} \bigg/ \left(\frac{D_{ML}}{t} \right)^{1/2} \gg 1, \tag{2}$$

where the parameter t labels the effective measurement time. The kinetic parameter $k_d(D_M/k_a c_L)^{1/2}$ has been compared to the diffusion parameter $(D_{ML}/t)^{1/2}$ and if condition (2) is fulfilled the consumption of ML is mass transport controlled by semi-infinite diffusion. The lability of the system depends also on the voltammetric method used to study the complexation properties because of different values of t [8].

If conditions (1) $c_L \gg c_M$, (2) $D_M \gg D_{ML}$, (3) the Davison criteria (for ASV technique) [9, 10]:

$$(k_d + k'_a)^{1/2} \, \delta/D_M^{1/2} \, K \gg 1,$$ (3)

where the diffusion layer thickness δ is a function of D_{ML} and $k'_a = k_a c_L$, and (4) the reduction of the metal ion, formed near the electrode by dissociation of ML is fast enough, are fulfilled, the complex is labile under experiment conditions and the stability constant K depends on the normalized current ϕ:

$$\phi = I_{\text{with ligand}}/I_{\text{without ligand}} = [(1 + \varepsilon K c_L)/(1 + K c_L)]^p.$$ (4)

Here ε denotes the relation of diffusion coefficients $\varepsilon = D_{ML}/D_M$, which are estimated in the literature as 0.019 and 0.023 for PAA and PMA, respectively [11]. Parameter p depends on the nature of the mass transport and is equal to 1/2 (semi-infinite diffusion) or 2/3 (laminar convective diffusion). The stability constant can be calculated according to the equation:

$$K = (\phi^{1/p} - 1)/(\varepsilon - \phi^{1/p})c_L.$$ (5)

Equation 5 is valid if only 1:1 complex is formed in the solution and the reaction is quasimonomolecular ($c_L \gg c_M + c_{ML}$). If $\varepsilon K c_L \ll 1$, Eq. 5 can be presented as

$$1/\phi^{1/p} = 1 + K c_L$$ (6)

and if the right p value ($p = 1/2$ for dropping mercury electrode or 2/3 in the case of rotating disc electrode) has been used, $1/\phi^{1/p}$ vs. c_L plots must be linear with the intercept 1 and the slope equal to K [12]. As for PMA and PAA ε is estimated in the literature to be approximately 0.02, the condition $K c_L \ll 50$ must be fulfilled.

The aim of this paper is to report results of studies of the dependence of complexes formed by Pb^{2+} with PMA and PAA on the pH value, counterion concentration, and charge using sampled direct current polarography (DCP), differential pulse polarography (DPP), and differential pulse anodic stripping voltammetry (DPASV) on static mercury drop electrode (SMDE), hanging mercury drop electrode (HMDE), and thin mercury film glassy carbon rotating disc electrode (RDE).

EXPERIMENTAL

Reagent grade PAA and PMA solutions from BDH laboratory (average molecular mass Mw = 230 000 and 26 000, respectively) were kindly presented by Professor Miquel Esteban (Department of Analytical Chemistry, University of Barcelona). These were used to prepare stock solutions with the concentration of carboxylic groups approximately 1 mol l^{-1}. The concentration was determined by conductometric and potentiometric acid–base titration. To 2 ml of the stock solution 20 ml of the MilliQ water was added and titrated with 0.1 mol l^{-1} NaOH under control of Orion 150 conductivity meter and Evikon pH meter (Tartu, Estonia). Both instruments were calibrated before measurement and the difference in the concentration for the methods used was about 2%. The degree of neutralization α_n was determined from potentiometric titration data.

All other reagents were Pro analysi or Suprapur grade, solutions were prepared using the MilliQ water. The test of supporting electrolyte solutions on heavy metal content using DPASV showed summary concentration of copper, lead, cadmium, and zinc lower than 10^{-8} mol l^{-1} in 0.1 mol l^{-1} solution. The detection limit for lead and cadmium was determined as 2×10^{-10} mol l^{-1}, for zinc 5×10^{-10} mol l^{-1} (DPASV, RDE, deposition time $\tau = 10$ min), and for copper 1×10^{-9} mol l^{-1} (cathodic DPSV with 8-hydroxyquinoline on HMDE, $\tau = 2$ min). Criteria for detection limit were chosen as standard deviation was less than 5% and $R^2 > 0.98$.

Voltammetric measurements were performed using the AUTOLAB system (Ecochemie) attached to a 663 VA Stand (Metrohm) with multimode mercury electrode and RDE by means of the software packages EAS 2 and GPES 3 (Ecochemie). A previously mercury-plated thin film glassy carbon electrode was used in RDE experiments. The formation of mercury film on the glassy carbon working electrode was provided from acidified to pH < 3 8×10^{-5} mol l^{-1} $Hg(NO_3)_2$ solution. The deposition time was 300 s at the electrode potential $E = -1.0$ V. To avoid hydrolysis of Hg^{2+} after plating the electrode was rinsed with diluted HNO_3 and water. The reference and auxiliary electrodes were Ag/AgCl, KCl (3 mol l^{-1}), and glassy carbon rod, respectively.

The concentration of Pb^{2+} was 10^{-4} mol l^{-1} (DCP, DPP) and 10^{-6} or 4×10^{-7} mol l^{-1} for DPASV measurements. For DCP and DPP the rather high lead concentrations, not really corresponding to the concentration in natural waters, were chosen because of the lower sensitivity of these methods. In DPASV experiments measurements were made with lead concentrations between 10^{-9} and 10^{-6} mol l^{-1} and a good agreement in stability constant values was observed. The results confirm the theoretical assumption about independence of K from the metal concentration if the condition $c_L \gg c_M$ is fulfilled.

During titration of Pb^{2+} with polyacids, the pH in the glass measurement cell was kept constant by adding 10^{-2} mol l^{-1} solutions of KOH or HNO_3. The value of pH in the cell was controlled by means of a pH-meter.

The pulse modulation time was 0.07 s, modulation amplitude 0.050 V, step potential 0.003 V, and interval time 0.30 s in differential pulse methods. The deposition potential for DPASV mode was chosen using pseudopolarograms and was -1.0 V for Pb^{2+}. The deposition time was 60 s for the RDE and HMDE measurements.

To eliminate oxygen and hydrocarbonates, 25 ml of the supporting electrolyte solution with addition of the metal stock solution was deaerated in the cell with Ar (99.995%) at pH < 4. After 25 min deaeration, pH was adjusted to the desired value and the voltammogram of the sample was registered. Aliquots of 10^{-2} or 10^{-1} mol l^{-1} polyacid solution, prepared from titrated stock solution, were added and I vs. E curve was registered after each addition. The experiment was finished after ϕ stayed approximately constant. The needed excess of ligand over the total lead concentration $c_T = c_{ML} + c_M$ was up to the ratio of c_L/c_T 10–20 in case of DPP and DCP or about 1000 for DPASV and it depended on the pH, concentration, and nature of the supporting electrolyte.

RESULTS AND DISCUSSION

Dependence of the stability of the Pb–PMA and Pb–PAA complexes on pH, counterion concentration, and charge was studied using voltammetric techniques on RDE (DPASV), HMDE (DPASV), and SMDE (DPP, DCP). $La(NO_3)_3$ (0.001–0.01 mol l^{-1}), $Ca(NO_3)_2$, and KNO_3 (0.01–0.5 mol l^{-1}) in the pH region of 3.5–7.0 were used as supporting electrolytes in order to characterize the screening effect and competition of cations in the formation of complexes. The studied pH and counterion concentration regions were limited by non-lability of the system at lower pH values and higher supporting electrolyte concentrations, whereas problems occurred because of hydrolysis of Pb^{2+} at higher pH values. Hydrolysis and adsorption of the products on the cell walls were notable already at pH = 4.5 as a decrease in the DPP or DPASV peak height in lead-supporting electrolyte solution. This process was quite slow and equilibrium arrived during 20–30 min. Using the solution exchange method in the cell we found that the desorption of lead into acidified solution took approximately the same time. In the presence of a large excess of polyacids we noted absence of the adsorption effect, i.e. after exchange of Pb^{2+} and ligand containing solution on the acidified supporting electrolyte no lead was observed in the cell.

Linear dependence of the limiting current I_{Lim} on the square root of the rotating frequency ω of the RDE shows a fast charge transmission process and the independence of normalized currents ϕ from ω and therefore from the diffusion layer thickness, indicating lability of complexes under the studied conditions. Addition of ligand caused depression of the limiting current (DCP) or peak current (DPP, DPASV). Typical normal shaped ϕ vs. c_L plots were obtained for all studied systems and experimental techniques used. Figure 1 presents ϕ vs. c_L dependencies for the Pb–PAA system at different Ca^{2+} concentrations
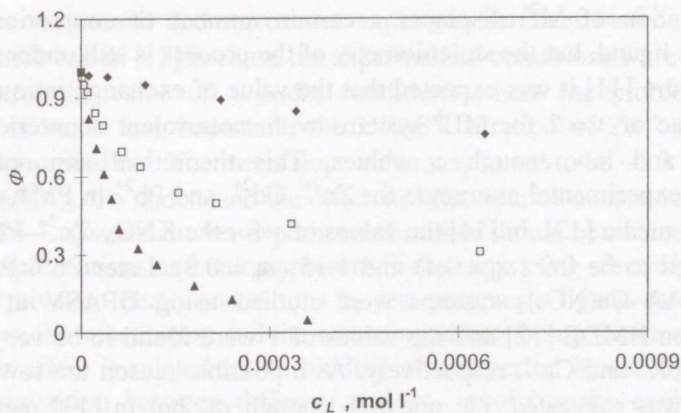
Fig. 1. Normalized peak current values as a function of PAA concentration at $Ca(NO_3)_2$ concentrations: 0.02 (◆), 0.07 (□), and 0.1 (▲) mol l^{-1} at RDE, DPASV mode. Pb^{2+} concentration 4×10^{-7} mol l^{-1}, pH = 4.75.

obtained under DPASV conditions on RDE and they are similar to those for Pb–PMA. In solutions containing KNO_3 the ϕ value was lower at the same cation concentration. All these results are in agreement with those expected theoretically according to the model. The stability of the PbL^+ complexes decreases with increasing concentration of the supporting electrolyte and cation charge, but increases with increasing pH (Table 1). The values of log K were calculated using Eq. 3 and determined from the slope of $1/\phi^{1/p}$ vs. c_L plots. Linear plots and good agreement in K values were observed between different polarographic techniques when the parameter p was chosen to be equal to 1/2 in the case of DCP and DPP on SMDE or 2/3 in DPASV measurements on HMDE and RDE. This means that for the HMDE in stirred solution in the mass transfer equation, the term $D^{2/3}$ should be used like in the Levich equation for RDE.

Table 1. Dependence of the stability constant K on pH of the supporting electrolyte cation at KNO_3 and $Ca(NO_3)_2$ concentration of 0.01 mol l^{-1}. Concentration of Pb^{2+} 10^{-4} (DCP, DPP), 10^{-6} (DPASV on RDE), and 4×10^{-7} mol l^{-1} (DPASV on HMDE). Differences between presented mean values of log K for different techniques are around 0.15 units

pH	log K			
	PMA		PAA	
	K^+	Ca^{2+}	K^+	Ca^{2+}
4.0	3.72	2.73	4.04	3.30
4.25	4.07	3.24	4.30	3.80
4.5	4.41	3.57	4.70	4.03
4.75	4.77	3.81	5.12	4.26
5.0	4.90	3.85	5.25	4.56
5.5	5.16	4.06	5.42	4.72
6.0	5.24	4.11	5.56	4.95
6.5	5.68	4.40	5.95	5.18
7.0	5.87	4.52	6.12	5.60

Complexation of M^{2+} displaces a certain number of counterions initially bound to the ligand, but the stoichiometry of the process is still under discussion. In the literature [11] it was expected that the value of exchange ratio can reach a limiting value of $\nu = 2$ for ML^+ systems with monovalent counterions at high enough α_n and low enough c_L values. This theoretical assumption found satisfactory experimental assurance for Zn^{2+}, Cd^{2+}, and Pb^{2+} in PMA–KNO$_3$ and PAA–KNO$_3$ media [13]. In [14] the values of ν for the KNO$_3$–Zn^{2+}–PMA system were reported to be 0.9 ($\alpha_n = 0.4$) and 1.15 ($\alpha_n = 0.8$). Later Pb^{2+}–PAA–KNO$_3$ and Pb^{2+}–PAA–Ca(NO$_3$)$_2$ systems were studied using DPASV at pH = 4.75 ($\alpha_n = 0.32$) on HMDE [12] and the values of ν were found to be very low, 0.46 and 1.34 for K$^+$ and Ca^{2+}, respectively. As a possible reason too low pH of the experiment was suggested, i.e. not high enough α_n, but in [13] measurements were carried out in the case of Pb^{2+} at the same $\alpha_n = 0.3$.

To estimate the exchange ratio ν between Pb^{2+} and counterions depending on their concentration and charge, the log K vs. log a (where a is the counterion activity) plots were constructed. Figure 2 presents plots for the studied systems under DPP experimental conditions at pH = 4.75. For all techniques the slopes were close to the values of ν published in [12]: −0.44 (PAA–K$^+$), −0.35 (PMA–K$^+$), −1.3 (PAA–Ca^{2+}), and −1.1 (PMA–Ca^{2+}). It was supposed that the results were affected by the hydrolysis and adsorption of the product Pb(OH)$^+$ onto the cell walls, but when the results were corrected for the adsorption phenomena [15, 16], no significant changes in log K vs. log a slopes were observed.

There is no doubt that ν_{KPb} is markedly different from its two potential limits, i.e., (a) zero in the absence of interaction between K$^+$ and polyacid and (b) two, in the case of complete charge compensation. Under the conditions of our voltammetric experiment, where $c_{Pb} \ll c_L$, complexation of the ligand by Pb^{2+}
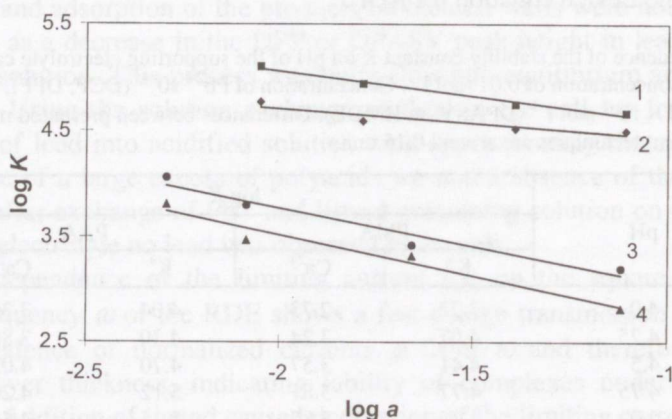

Fig. 2. Formation constant values as a function of counterion activity a in Pb–PAA–K$^+$ (1), Pb–PMA–K$^+$ (2), Pb–PAA–Ca^{2+} (3), and Pb–PMA–Ca^{2+} (4) systems, obtained at SMDE, DPP mode. Pb^{2+} concentration 10^{-4} mol l^{-1}, pH = 4.75.

was always very small and we cannot explain differences between the results presented here and in [13] because the experimental conditions were very similar.

To control the value of ν under conditions where the problem of cation hydrolysis is much less important, the DPASV titration of Zn^{2+} with PAA at $\alpha_n = 0.6$ was carried out. The mean slope value was found to be -1.3 in KNO_3 and -1.4 in $Ca(NO_3)_2$. To understand the different behaviour of monovalent cations on Pb–L and Zn–L systems further experimental studies should be carried out.

In principle, cations and anions present in the supporting electrolyte affect the binding of bivalent heavy metal ions by the polymeric ligand through several mechanisms, the substitution and the screening effects being the most significant. The former effect is related to the binding of counterion by the ligand and the further competition between different cations, involving the exchange of the heavy metal from the complex. The latter effect is related to the accumulation of free counterions in the diffuse layer around the polyelectrolyte, controlling the effective charge density of the macromolecule, which also affects the ion exchange. This may be the reason for the decrease in the log K values when the counterion concentration increases. The question concerning the M–L interaction and exchange ratio is more complicated in the case of bi- or threevalent supporting cations because of stereometrical problems, i.e. if possible different complexes, for example —$COOCa^+$ or —$COOCaOOC$—, are formed.

It must be noted that if La^{3+} is a counterion, the system tends to flocculate/precipitate at higher pH values than 3.8–3.9, depending on the ion concentration. At the same time the differences observed between the K values calculated at pH = 3.6 and 4.0, were not great, although the correlation was essentially lower than the usual range of $R^2 = 0.96$–1.0. Today we do not yet know the properties of these colloidal particles, but if we suppose that the diffusion coefficient is not very different from that of the PbL^+ complex, a significant decrease in K, i.e. a rise of the screening effect, was observed in the case of La^{3+} as the counterion. For example, in solutions with the activity of K^+, Ca^{2+}, and La^{3+} $a = 0.01$, the log K values were 4.75, 3.9, and 3.1, respectively, in Pb^{2+}–PMA system at pH = 4.75.

Studies at different pH values within the range of 3.5–7 showed a decrease in normalized currents with increasing pH, i.e. α_n, which means a rise in the stability of complexes at higher pH values. Plots of ϕ vs. c_L for Pb–PAA are shown in Fig. 3. The theory of labile complexes was elaborated presuming that only the neutralized acid as a ligand participates in the complex formation [5, 6], which means that the degree of neutralization α_n has an important role in the calculations of stability constants. The dependence of α_n on pH was determined by means of potentiometric acid–base titration. The $d\alpha_n/dpH$ slope can be calculated from the Henderson–Hasselbach equation as equal to 0.4 and the plots are parallel for acids with different dissociation constant K_d. From the experimental titration curves the slope was found to be 0.38 for PMA ($K_d = 1.25 \times 10^{-5}$) and 0.2 for PAA ($K_d = 2 \times 10^{-5}$).
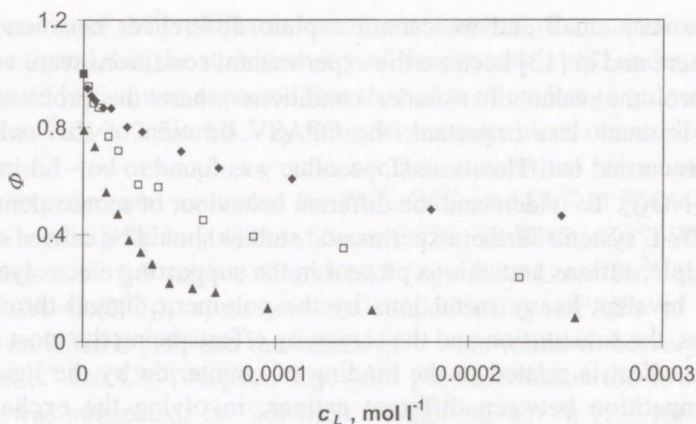
Fig. 3. Dependence of the normalized current in Pb–PAA system on PAA concentration at different pH values: pH = 4.25 (◆), 4.50 (□), and 4.75 (▲) at RDE, DPASV mode. Pb^{2+} concentration 4×10^{-7} mol l^{-1}, 0.1 mol l^{-1} KNO_3.

The constructed $\log K/\alpha_n$ like $\log K$/pH plots are linear at α_n values higher than 0.1 (PMA) or 0.3 (PAA). In both supporting electrolytes plots are more or less parallel in this α_n region with lower $\log K$ values in $Ca(NO_3)_2$. At lower α_n the stability constant decreases steeply. The curvature of the $\log K/\alpha_n$ dependencies at lower α_n and increasing K with pH is typical of polyacidic ligands, i.e. the observed K increases with increasing charge due to growing electrostatic contribution to the overall Gibbs energy of binding. The lowering of the slope with increasing α_n reflects the transition into a more expanded conformation. For a given α_n, the charge density of the polyionic species is thus reduced and consequently the strength of metal ion binding increases less strongly with increasing degree of neutralization.

Though the concentration of the anionic form of polyacids was used for the calculation of the stability constant, dependencies of $\log K$ vs. pH have slopes 0.5 ± 0.05 for PMA and PAA in 0.01 mol l^{-1} KNO_3. When 0.01 mol l^{-1} $Ca(NO_3)_2$ was used as supporting electrolyte, the slopes were similar, 0.5 and 0.65, respectively (Fig. 4). As the slope does not depend essentially on the supporting cation concentration and charge, it was supposed that there exists some exchange between non-neutralized carboxylic groups and Pb^{2+} though this assumption needs additional experimental data.

SUMMARY

Our study of the complex formation of Pb^{2+} with polycarboxylic acids PAA and PMA using different polarographic techniques (DPASV, DPP, DCP) on dropping mercury and thin film glassy carbon rotating disc electrodes showed the
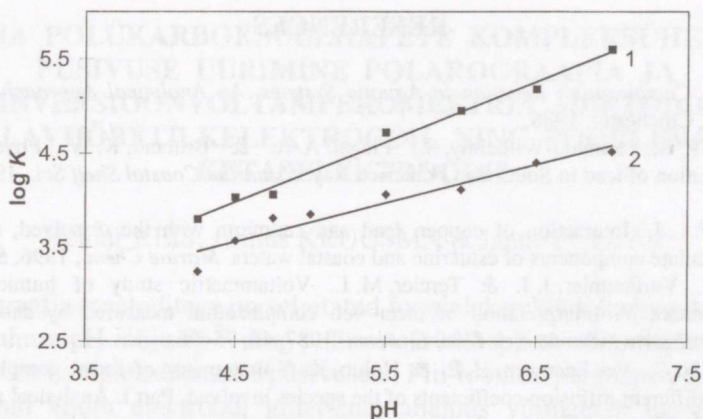
Fig. 4. Dependence of the stability constant on pH in Pb–PAA (1) and Pb–PMA (2) systems, measured at SMDE, DPP mode. Pb^{2+} concentration 10^{-4} mol l^{-1}, 0.01 mol l^{-1} $Ca(NO_3)_2$.

complexes to be labile in the pH range of 3.5–7 in 0.01–0.5 mol l^{-1} KNO_3 and $Ca(NO_3)_2$ as the supporting electrolyte solutions and the charge transfer process fast enough on the used time scale. This allowed us to calculate the stability constant of macromolecular complexes. Solution exchange experiments showed desorption of hydrolyzed lead species from the cell components in the case of an excess of the ligand. The exchange ratio values between the supporting electrolyte cations and complexed Pb^{2+} were determined and found to be lower than presented in the literature.

The both supporting electrolytes log K/α_n and log K/pH plots are linear at α_n values higher than 0.1 (PMA) or 0.3 (PAA). The curvature of the log K/α_n dependencies at lower α_n and increasing K with pH could be explained with the transition into a more expanded conformation, with increasing charge and growing electrostatic contribution to the overall Gibbs energy of binding.

Dependencies of log K *vs.* pH have slopes 0.5±0.05 for PMA and PAA in 0.01 mol l^{-1} KNO_3. In 0.01 mol l^{-1} $Ca(NO_3)_2$ the slopes were similar, 0.5 and 0.65, respectively. It was supposed that there exists some exchange between non-neutralized carboxylic groups and Pb^{2+} though additional experimental data are needed to confirm this assumption.

ACKNOWLEDGEMENT

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PLII JA POLÜKARBOKSÜÜLHAPETE KOMPLEKSÜHENDITE PÜSIVUSE UURIMINE POLAROGRAAFIA JA INVERSIOONVOLTAMPEROMEETRIA MEETODIL ELAVHÕBETILKELEKTROODIL NING PÖÖRLEVAL KETASELEKTROODIL

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Polarograafia meetoditega on selgitatud foonielektrolüüdi laengu, kontsentratsiooni ja lahuse pH mõju Pb^{2+} ning polümetakrüülhappest või polüakrüülhappest moodustuvate kompleksühendite püsivusele. Plii-ioonide polühapetega tiitrimisel registreeritud voolu elektroodi graafikute analüüs võimaldab täpselt määrata vastavate kompleksühendite püsivuskonstante K. Arvutuslik ja meie poolt leitud graafiline meetod püsivuskonstantide määramiseks annavad hästi kokkulangevaid tulemusi, kui kasutada õigeid massiülekandekoefitsiente: 1/2 tilkuva elektroodi tehnikate puhul ning 2/3 pöörleval ketaselektroodil ja inversioonvoltamperomeetria korral statsionaarsel tilkelektroodil segatavas lahuses. Pb^{2+} ja foonikatioonide vahetuskoefitsientide määramisel $\log K$ ja elektrolüüdi aktiivsuse logaritmi sõltuvusest ilmnes, et sirgete tõus on $-0{,}5$ (K^+) ja $-1{,}2$ (Ca^{2+}) lähedal. See on K^+ korral tunduvalt madalam kui kirjanduses toodud; Ca^{2+} jaoks kirjanduses andmeid pole. Kuna teooria kohaselt osaleb kompleksimoodustumisreaktsioonis vaid happe anioonne vorm, kasutati K arvutamisel ligandi kontsentratsioonina happe kontsentratsiooni ja neutralisatsiooniastme α_n korrutist, α_n määrati happe potentsiomeetrilise tiitrimiskõvera alusel ja see kasvab pH tõusuga. Uurides püsivuskonstandi olenevust lahuse pH väärtusest ilmnes, et nii $\log K$-α_n kui ka $\log K$-pH sõltuvused on sirged alates α_n väärtusest $0{,}1$–$0{,}3$ olenevalt happe dissotsiatsioonikonstandist, madalamatel pH-del toimub püsivuskonstandi järsk vähenemine. Sellist sõltuvust on seletatud makromolekuli laengutiheduse muutusega pH kasvades, mis teatud α_n-st muudab polühappe molekuli konformatsiooni ja edaspidine lineaarne $\log K$ kasv on seotud metall-ligandi sideme Gibbsi energia muutusega laengutiheduse kasvades.