

Application of ASV for Trace Metal Speciation IV. Determination of Lead-Chloride Stability Constants by Rotating Mercury Coated Glassy Carbon Electrode

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The stability constants of lead-chloride complexes were determined by the neopolarographic method using rotating mercury coated glassy-carbon electrode. The results were compared with the literature and discussed.

INTRODUCTION

Neopolarography, the new anodic stripping voltammetry method for trace metal speciation, has been described in detail in the literature^{5,6} and in the previous papers of this series¹⁻³. Although new, the method has been successfully applied to the determination of the chloro-, carbonato- and hydroxo-complexation constants of the lead and cadmium in seawater^{1,4,5}. After the theoretical work of Turner and Whitfield⁶, the method is no longer only empirical.

The principles of neopolarography using a rotating, mercury covered, glassy-carbon electrode⁷ have been described in our previous work³. The main objective of this paper is to report on the results of the application of this electrode in the determination of lead-chloride stability constants in acidified, constant strength, ionic medium (perchlorate) at the lead concentration of 10^{-8} mol dm⁻³.

Generally, in the case of very fast, reversible reactions of complexation, the concentration of the metal ion can be expressed as follows:

$$c_{M^+} = \frac{c_{ox}}{B + 1}$$

where:

$$c_{ox} = c_{M^+} + \sum_{j=1}^n c_{MX_j}$$

$$B = \sum_{j=1}^n \beta_j c_X^j$$

$$\beta_j = \frac{c_{MX_j}}{c_M c_X^j}$$

* Taken in part from M. Sc. thesis of M. L., University of Zagreb, 1977.

By the addition of term B to a previously developed formula³ the integrated cathodic current during accumulation may be calculated as:

$$I = I_g (B + 1)^{-1} l \delta D_{\text{ox}}^{-1} T^{-1} e^{-\varphi} (1 - e^{-UT}) \varepsilon \quad (1)$$

where

$$I_g = D_{\text{ox}}^{1/2} \delta^{-1} T$$

$$\varphi = -\frac{nF}{RT} (E - E^0)$$

$$U = D_{\text{ox}} (B + 1) l^{-1} \delta^{-1} e^{\varphi}$$

$$\varepsilon = \exp(\Lambda_B^2 t_1) \operatorname{erfc}(\Lambda_B t_1^{1/2})$$

$$\Lambda_B = (B + 1) e^{\varphi} D_{\text{ox}}^{1/2} l^{-1}$$

T = the time of accumulation

δ = the thickness of the diffusion layer

l = the thickness of the mercury film at the electrode
(all other symbols have their usual meanings)

The logarithmic analysis of eq. (1) gives

$$\ln \frac{I_g - I}{I} = -\frac{nF}{RT} (E - E^0) + \ln \frac{l \delta}{D_{\text{ox}} T}$$

$$- \ln(B + 1) + \ln \varepsilon + \ln(1 - e^{-UT}) - \ln(1 - \varepsilon Z) \quad (2)$$

where

$$Z = (B + 1)^{-1} \frac{l \delta}{D_{\text{ox}} T} e^{-\varphi} (1 - e^{-UT})$$

As has been already proved, the influence of the last three terms on the logarithmic analysis of the two-electron, reversible neopolarograms is negligible. The half-wave potential of eq. (2) can thus be expressed from the first three terms:

$$(E_{1/2}^*)_{\text{C}} = E^0 + \frac{nF}{RT} \ln \frac{l \delta}{D_{\text{ox}} T} - \frac{nF}{RT} \ln(B + 1) \quad (3)$$

or

$$(E_{1/2}^*)_{\text{C}} = (E_{1/2}^*)_{\text{S}} - \frac{nF}{RT} \ln \left(1 + \sum_{j=1}^n \beta_j c_x^j \right)$$

Equation (4) enables us to use the method of DeFord and Hume⁸ for the evaluation of complex constants from the shift of half-wave potentials of neopolarograms, depending on the ligand concentration.

EXPERIMENTAL

The instrumental and experimental conditions were the same as described in the preceding paper³.

For these experiments, a 5.0 mol dm⁻³ solution of NaCl from »Merck« — supra purr. reagent was prepared and pre-electrolized during 24 hours at -1.3 (V) vs. SCE.

Two different Pb²⁺ — Cl⁻ solution systems were prepared:

1. $\text{Pb}(\text{NO}_3)_2 - \text{NaClO}_4 - \text{HClO}_4 - \text{NaCl} - \text{HgCl}_2$ (8 solutions) $\text{pH} = 2$; ionic strength = 0.7 mol dm^{-3} ; conc. NaCl between $1 \cdot 10^{-4}$ and 0.7 mol dm^{-3} ;
2. $\text{Pb}(\text{NO}_3)_2 - \text{NaClO}_4 - \text{HClO}_4 - \text{NaCl} - \text{HgCl}_2$ (20 solutions) $\text{pH} = 2$; ionic strength = 3.0 ; conc. NaCl between $1 \cdot 10^{-3}$ and 3.0 mol dm^{-3} .

In all the solutions the concentrations of $\text{Pb}(\text{NO}_3)_2$ and HgCl_2 were $2 \cdot 10^{-3}$ and $2 \cdot 10^{-5} \text{ mol dm}^{-3}$, respectively.

Some of experiments were performed with seawater acidified to $\text{pH} = 2$ and kept in polyethylene bottles.

Control measurements were made using d.c. polarography at the dropping mercury electrode. The system $\text{Pb}(\text{NO}_3)_2 - \text{NaCl} - \text{NaClO}_4 - \text{HClO}_4$ was prepared with chloride concentration between $1 \cdot 10^{-4}$ and 3.0 mol dm^{-3} . The ionic strength of the solutions was 0.7 . The concentration of Pb^{2+} was $1 \cdot 10^{-4} \text{ mol dm}^{-3}$ and the pH was 2 in all the solutions. Recording was made between -0.5 (V) and -0.65 (V) vs. the SCE, the speed of the changing potential was 1 mV/s , the drop time was 4 (s) and height of the reservoir was 30 (cm).

RESULTS AND DISCUSSION

Figure 1 presents the results of all the measurements. The lower curve shows the relationship between the d.c. polarographic $E_{1/2}$ and the log. conc. Cl^- , while the upper two curves illustrate the same correlation for the neopolarographic $E_{1/2}^*$. The highest curve corresponds to the ionic strength of 0.7 and the curve beneath it corresponds to the ionic strength of 3.0 . A reciprocal similarity of these curves may be observed, but also their dependence on the kind of electrode used and the ionic strength of solution. The square point on the first curve represents the value obtained by the measurement of seawater. This point is dovetailed in all other results and this might be a proof that the complex-formation constant values calculated from this experiment correspond to the values of the constants actually present in the seawater

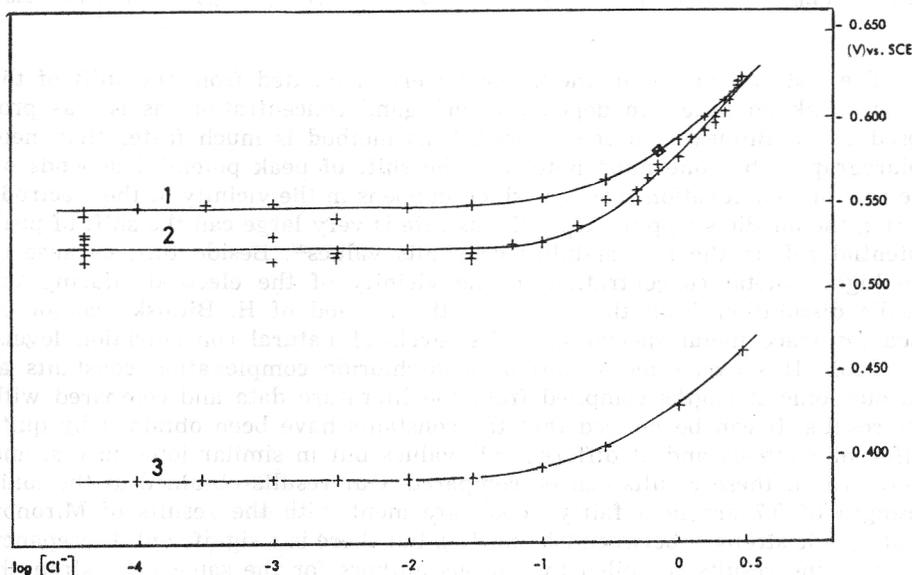


Figure 1. A comparison of the neopolarographic and d.c. polarographic results of the measurements of the shifting of half-wave potentials in relation to chloride ion concentration.

1 — neopol. i. s. = 0.7

2 — neopol. i. s. = 3.0

3 — d. c. pol. i. s. = 0.7

and that the ionic species of lead found in the experimental solutions exist in the seawater, as well.

Table I shows complexing constants values calculated from the data quoted by the DeFord-Hume method⁸ and the values obtained by the least square method calculated by a computer²². Some discrepancies between the results obtained by these two methods, especially where the last constant is concerned, were observed. The least square method was favored because of its less pronounced subjectivity.

TABLE I

The stability constants of lead-chloride complexes.

DeF-H — DeFord-Hume method of calculation

l. sq. m. — »least square« statistical method of calculation

Experimental method	Calculation method	Ionic strength	β_1	β_2	β_3	K_1	K_2	K_3
		mol dm ⁻³						
D. c. polarogr.	DeF—H	0.7	7	15	7.4	7	2.1	0.5
"	l. sq. m.	"	6.8±0.6	15.4±2.1	7.3±0.9	6.8	2.3	0.47
neopolarography	DeF—H	0.7	6	11.2	7	6	1.9	0.6
"	l. sq. m.	"	4.9±1.5	12.5±4.1	5.6±1.9	4.9	2.5	0.45
neopolarography	DeF—H	0.3	5	25	55	5	5	2.2
"	l. sq. m.	"	4.1±1.8	17.7±8.3	51.8±5.8	4.1	4.3	2.9
ASV — ΔE_p	DeF—H	0.7	8	18	5.5	8	2.25	0.3
ASV — ΔE_p	DeF—H	0.3	5	24	61.5	5	4.8	2.5

The last two values in the Table I were calculated from the shift of the anodic peak potentials in dependence on ligand concentration, as is proposed by H. Bilinski and coworkers²¹. This method is much faster than neopolarography, but one must note that the shift of peak potential depends on the rate of complexation reaction which happens in the vicinity of the electrode during the anodic stripping. Only if this rate is very large can the shift of peak potential reflect the real stability constants values²³. Beside this, because of the higher metal concentration in the vicinity of the electrode during the anodic dissolution from the amalgam, the method of H. Bilinski cannot be used for trace metal speciation at its levels of natural concentration levels.

Table II shows some values of lead-chloride complexation constants at various ionic strengths compiled from the literature data and compared with our results. It can be noticed that the constants have been obtained by quite different methods and at different pH values but in similar ionic media, and therefore all these results can be compared. Our results obtained at the ionic strength of 0.7 are in a fairly good agreement with the results of Mironov et al.⁹ (ionic strength between 0.5 and 1.0), but there is a significant discrepancy between the results compiled by various authors for the same ionic strength. Our results for the second and the third constant at the ionic strength of 3.0 are also in concordance with the literature, but the values for the first constant are notably lower. We do not know the reason for this discrepancy, but it should be pointed out that our measurements were performed at the concen-

TABLE II
Comparison of the Literature Data with the Stability Constants of the Lead-chloride Complexes Calculated from this Work

μ mol dm ⁻³	pH	t/°C	Method	Medium	[Pb ²⁺] (M)	Constants				Reference
						K ₁	K ₂	K ₃	K ₄	
—	—	25	pot.	Li(ClO ₄ —Cl)	—	35.6	2.0	7.05	—	10
0.1	7	25	kinet.	Na(ClO ₄ —Cl)	1·10 ⁻²	17.0	—	—	—	20
0.25	3	25	M(Hg)	"	1·10 ⁻³	10	3	—	—	9
0.5	3	25	"	"	1·10 ⁻³	6.8	2	—	—	9
0.7	2	25	ASV	"	2·10 ⁻⁸	27	—	—	—	2
0.7	2	20	d.c. pol.	"	2·10 ⁻⁴	7	2.1	0.5	—	This work
0.7	2	20	d.c. pol.*	"	2·10 ⁻⁴	6.8	2.3	0.47	—	This work
0.7	2	20	ASV ($\Delta E_{1/2}$)	"	2·10 ⁻⁸	6	1.9	0.6	—	This work
0.7	2	20	ASV* ($\Delta E_{1/2}$)	"	2·10 ⁻⁸	4.9	2.5	0.45	—	This work
0.7	2	20	ASV (ΔE_p)	"	2·10 ⁻⁸	8	2.25	0.3	—	This work
0.75	3	25	M(Hg)	"	1·10 ⁻³	7.0	4.1	0.55	—	9
1.0	3	25	M(Hg)	Na(ClO ₄ —Cl)	1·10 ⁻³	8.0	2.9	1.2	—	9
1.0	5	25	a.c. pol.	"	4·10 ⁻⁴	15.0	1.0	5.3	—	12
1.0	5-6	25	d.c. pol.	"	4.5·10 ⁻⁴	9.1	0.81	3.2	—	13
1.0	—	25	"	"	—	26.8	6.75	0.66	1.17	15
1.0	7	23	kinet.	"	5·10 ⁻²	12.0	—	—	—	20
1.0	0	20	cix. sol.	H(ClO ₄ —Cl)	—	65.0	—	—	—	16
2.0	3	25	M(Hg)	Na(ClO ₄ —Cl)	1·10 ⁻³	10.0	2.6	1.15	0.12	9
2.0	5-6	25	d.c. pol.	"	4.8·10 ⁻⁴	15.2	0.92	2.2	—	14
3.0	6	25	sol.	Li(ClO ₄ —Cl)	0.1	16.0	—	—	—	11
3.0	3	25	M(Hg)	"	1·10 ⁻²	15.0	3.47	1.93	1.1	18
3.0	0	25	"	"	1·10 ⁻³	15.5	3.46	2.0	0.07	18
3.0	2	20	ASV ($\Delta E_{1/2}$)	Na(ClO ₄ —Cl)	2·10 ⁻⁸	5	5	2.2	—	This work
3.0	2	20	ASV* ($\Delta E_{1/2}$)	"	2·10 ⁻⁸	4.1	4.3	2.9	—	This work
3.0	2	20	ASV (ΔE_p)	"	2·10 ⁻⁸	5	4.8	2.5	—	This work
3.0	—	25	M(Hg)	"	—	11.2	2.9	2.1	—	17
3.0	3	25	"	"	1·10 ⁻³	14.5	3.45	1.9	0.05	9
3.0	3	25	"	Li(ClO ₄ —Cl)	1·10 ⁻³	16.0	3.1	1.9	0.13	18
3.0	3	25	sol.	"	5·10 ⁻³	17.0	4.35	1.3	0.55	18
4.0	3	25	M(Hg)	"	1·10 ⁻²	17.0	3.1	2.3	0.18	18
4.0	3	25	"	Na(ClO ₄ —Cl)	1·10 ⁻³	20.0	7.5	1.8	0.33	9
4.0	—	25	"	"	—	17.4	3.1	2.6	0.18	17
4.0	<0	25	sol.	H(ClO ₄ —Cl)	>1·10 ⁻⁴	10.0	29.3	<0.4	>3.5	19

* constants calculated by the least square method

tration level of 10^{-8} mol dm $^{-3}$, while all the other authors used the concentration range between 10^{-4} and 10^{-2} mol dm $^{-3}$. Apart from this discrepancy, we believe that our results are supported by the literature data and that this work affirms neopolarography as very convenient method for the detection of complexation constants detection at very low concentration of central metal atoms.

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SAŽETAK

Određivanje konstanti stabilnosti olovnih kompleksa s pomoću neopolarografske metode na rotacijskoj disk-elektrodi prekrivenoj živom

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Neopolarografskom metodom na rotacijskoj disk-elektrodi prekrivenoj tankim slojem žive određene su konstante stabilnosti kloro-kompleksa olova. Rezultati su uspoređeni s literaturnim podacima i opažene razlike prediskutirane.

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