Pb(II) complex formation in alkaline solutions of β-cyclodextrin

Eugenijus Norkus*[a], Giedrė Grincienė[a] and Rimantas Vaitkus[b]

[a]*Institute of Chemistry,*
A. Goštauto 9,
LT-2600 Vilnius, Lithuania
[b]*Vilnius Pedagogical University,*
Studentų 39,
LT-2034 Vilnius, Lithuania

Polarographic and UV-spectrophotometric investigations of Pb(II) complex formation with β-cyclodextrin showed that the complexation of Pb(II) ions begins at pH over 10. The possibility of the formation of lead(II) 1:1 complex with β-cyclodextrin anion was shown within the pH range from 9.7 to 12.0. The logarithm of the stability constant of this complex compound is equal to 16.7 ± 0.2 (20 °C, ionic strength 1.0, 4.4 mM β-cyclodextrin, $11.0 < \mathrm{pH} < 12.0$) and the molar extinction coefficient value is *ca.* 5500 (λ_{max} = 260 nm). With further increase in solution pH the Pb–β-cyclodextrin complex decomposes and converts to Pb(II) hydroxy-complexes. This process occurs with a decrease in Pb(II) complexation degree. The latter result could be explained by a decrease in the β-cyclodextrin anion activity. The results show that $Pb(OH)_3^-$ encapsulation into β-CD cavity does not occur.

Key words: cyclodextrin, lead(II), complex formation

INTRODUCTION

Cyclodextrins (CD) inclusion complex formation with different compounds is well known and investigated [1, 2]. On the contrary, the information about cyclodextrin interaction with heavy metal ions in aqueous solutions is rather scanty. Most thoroughly investigated are Cu(II) complexes with CD. Data about 2:1 and 1:1 Cu(II)–β-CD complex compounds are given in [3–8]. The complexation of other metal ions with CD is less investigated. A Mn(III)–β-CD complex also having a 2:1 ratio was reported in [9, 10]. The synthesis and characterization of 2:1 Cr(III), Co(II), Cu(II) and Ni(II) complexes with β-cyclodextrin is described in [11]. It must be noted that the data obtained are only qualitative and do not give information about the stability of the complexes in aqueous solutions.

Since the preliminary results showed the interaction of Pb(II) with β-cyclodextrin in alkaline solutions [12], the aim of this work was to investigate the interaction of Pb(II) ions with β-CD by means of polarography and UV-spectrophotometry, as well as to evaluate the β-cyclodextrin complexing ability in alkaline solutions.

EXPERIMENTAL

Materials

Analytical grade chemicals were used, and β-cyclodextrin (M_r = 1135) was *purum* from Fluka. $NaNO_3$ and NaOH solutions were used to keep ionic strength (*J*) of the solutions constant and equal in polarographic experiments to 1 M.

D.c. polarography

The polarographic curves were recorded by a *PU–1* polarograph, using a dropping mercury electrode in a thermostated three-electrode cell at 20 ± 0.1 °C. The potential scanning rate was 100 mV/min. The capillary characteristics were as follows: m = 2.95 mg s^{-1}, t = 3.73 s. The reference electrode was an Ag/AgCl electrode filled with a saturated KCl solution (the results of polarographic investigations are given *vs.* this electrode). The solutions were deaerated by bubbling Ar through the solution.

The values of the diffusion coefficient (*D*) were calculated using the Ilkovič equation [13]:

$$D^{1/2} = \frac{\bar{i}_{\mathrm{dif}}}{607ncm^{2/3}t^{1/6}}, \qquad (1)$$

---

*Corresponding author.

where $\bar{i}_{dif}$ is the limiting diffusion current (μA), c is the total concentration of Pb(II) ions (mM), m is the flow rate of Hg (mg s^{-1}), t is the time of the drop formation (s).

The values of the actual half-wave potential $E_{1/2}$ were determined within ± 1 mV from the plot of $\log(\bar{i}/\bar{i}_{\lim} - \bar{i}))$ against E.

Corrections for a decrease in $\bar{i}_{\lim}$ were made in the calculation of the half-wave potential shift ($\Delta E_{1/2}$) in the case of complex formation [13]:

$$\Delta E_{1/2} = (E_{1/2})_{compl} - (E_{1/2})_{free} - \\ -2.303\frac{RT}{nF}\log\sqrt{\frac{\bar{i}_{\lim free}}{\bar{i}_{\lim compl}}}, \qquad (2)$$

Corrections for the liquid-junction potential between alkaline solutions (pH > 13) and the saturated KCl solution in the Ag/AgCl reference electrode were introduced. The values of this potential were taken from [14].

The values of $\Delta E_{1/2}$ were used in the calculations of the parameters of lead(II) complexes according to [13]:

$$\sum_{x_i,y=0}^{N} \beta_{x_i y_i}\left[L^{n-}\right]^{x_i} a_{OH^-}^{y_i} = \\ = \exp\left[(nF/RT)\left(-\Delta E_{1/2}\right)\right] - 1, \qquad (3)$$

where $[L^{n-}]$ is an equilibrium concentration of the deprotonized form of β-cyclodextrin, and a stands for activity of OH$^-$ ions.

The concentration of free (uncomplexed) Pb^{2+} ions was calculated from $\Delta E_{1/2}$:

$$\text{pPb} = nF/2.303RT(-\Delta E_{1/2}) - \log[\text{Pb(II)}]_0, \qquad (4)$$

where $[\text{Pb(II)}]_0$ is the total Pb(II) concentration.

UV-spectrophotometry

The UV-spectra were recorded with a Perkin Elmer *Lambda 35* UV/VIS spectrometer at 20 °C in 1 cm-thick quartz cells. The comparison solution was water.

The molar extinction coefficient values of the individual complexes were calculated at λ_{max} according to:

$$\varepsilon_{\lambda_{max}} = A_{\lambda_{max}}/cl, \qquad (5)$$

where c is concentration (M) of the complexes, $A_{\lambda_{max}}$ is the light absorbance at wavelength λ_{max}, l is the cell width (cm).

pH-metric measurements

Measurements of the solutions pH were carried out with the aid of a Toledo Mettler *MP 220* pH-meter.

RESULTS AND DISCUSSION

Lead(II) forms no complexes with β-CD at pH < 9, even if there is a considerable excess (70 times) of β-CD in the solution. Formation of the Pb(OH)$_2$ precipitate is visually observed in the solution at pH 8–9 (this fact is in accordance with the values of the solubility product of Pb(OH)$_2$ given in [15] – they are in the range of 10^{-14} to 10^{-16}), and there is actually no polarographic wave of Pb(II) reduction.

The Pb(II) reduction wave is observed at higher pH values. In the pH range from 10 to *ca.* 11.5 the polarographic waves of Pb(II) reduction in alkaline β-CD solutions shift to more negative potentials (Fig. 1). This fact can be attributed to the deprotonation of β-CD in alkaline solutions (pK_a = 12.2 [16, 17]) and herewith to strengthening of β-CD complexing ability and complex formation. Thus we can conclude that undissociated β-CD does not interact with Pb(II) ions, but the deprotonated β-CD participates in complex formation with Pb(II) ions. The same tendency was observed when investigating Cu(II) complex formation with other carbohydrate – saccharose [18, 19] having a similar value of the deprotonation constant equal to 12.43 [20]. It must be noted that the formation of a large size complex compound is confirmed by an appreciable decrease

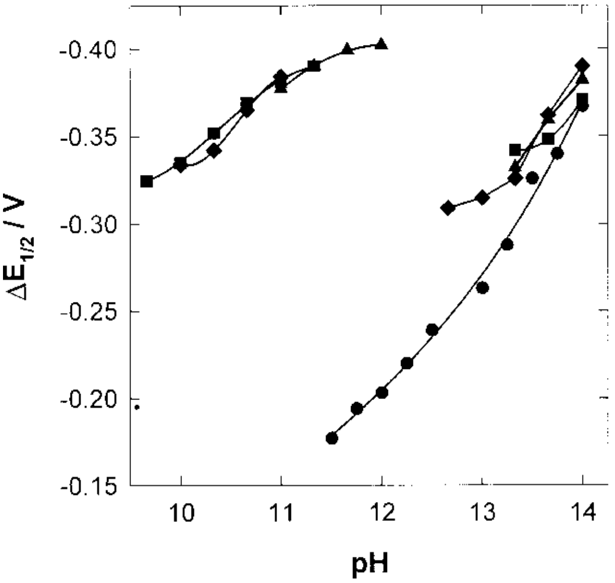

Fig. 1. Dependence of Pb(II) reduction half–wave potential shift ($\Delta E_{1/2}$) on solution pH. Solution composition (mM): $[\text{Pb(II)}]_0$ – 0.5; [β-cyclodextrin]$_0$: ▲ – 4.4, ■ – 22.0, ◆ – 35.2, ● – 0; J = 1; 20 °C

in the limiting current of Pb(II) reduction in the presence of β-CD (Table 1).

Before interpretation of the polarographic results the analysis of polarographic waves obtained was performed. It was found that the most limiting currents of Pb(II) reduction in alkaline solutions of β-CD are diffusion controlled. This was demonstrated by measurements at different temperatures and different heights of the mercury column – the limiting current dependence on the square root of the mercury column height is linear and the temperature coefficient of the limiting current is rather small and equal to *ca.* 1% per 1 °C (Fig. 2). The slope of the dependence of $\log(i/i_{\text{lim}}-i)-E$ of polarographic waves under investigation is 29–30 mV, showing a reversible two-electron Pb(II) reduction.

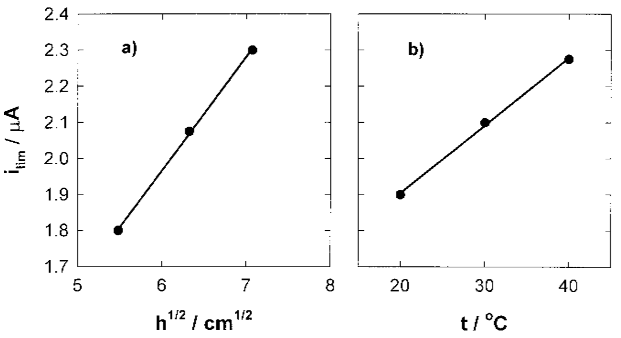

Fig. 2. Dependence of the limiting current of Pb(II) reduction in the presence of β-cyclodextrin on the square root of mercury column height (*a*) and temperature (*b*). Solution composition (mM): $[\text{Pb(II)}]_0$ – 0.5; [β-cyclodextrin]$_0$: – 25.0 ; J = 1

Table 1. **Characteristics of the process of Pb(II) reduction on a droping mercury electrode ($[\text{Pb(II)}]_0$ = 0.5 mM; J = 1; 20 °C)**

β-cyclodextrin, mM	pH	i_{lim}, μA	$-E_{1/2}$, V	$-\Delta E_{1/2}$, V
0	4.00	4.95	0.357	
0	11.50	3.2	0.529	0.177
	11.75	3.9	0.549	0.194
	12.00	4.3	0.559	0.203
	12.25	4.5	0.576	0.220
	12.50	4.7	0.596	0.239
	12.75	4.8	0.620	0.263
	13.25	5.6	0.644	0.288
	13.50	5.6	0.680	0.326
	13.75	5.5	0.690	0.340
	14.00	5.6	0.715	0.367
4.4	11.00	2.5	0.730	0.377
	11.33	2.4	0.742	0.390
	11.66	2.1	0.751	0.399
	12.00	2.1	0.754	0.402
	13.33	2.9	0.683	0.332
	13.66	3.7	0.709	0.359
	14.00	3.9	0.728	0.382
22.0	9.66	2.0	0.676	0.325
	10.00	2.0	0.686	0.335
	10.33	2.1	0.704	0.352
	10.66	2.0	0.720	0.369
	11.00	1.9	0.732	0.381
	11.33	1.8	0.740	0.390
	13.33	2.5	0.692	0.342
	13.66	2.8	0.696	0.348
	14.00	3.2	0.715	0.371
35.2	10.00	1.7	0.684	0.334
	10.33	1.7	0.692	0.342
	10.66	1.7	0.715	0.365
	11.00	1.5	0.733	0.384
	12.33	1.3	0.633	0.286
	12.66	1.4	0.658	0.309
	13.00	1.7	0.665	0.315
	13.33	2.4	0.675	0.326
	13.66	2.7	0.710	0.362
	14.00	3.0	0.734	0.390

The exceptions were observed at $12.0 < \text{pH} < 13.3$ (4.4 mM β-CD), $11.3 < \text{pH} < 13.3$ (22.0 mM β-CD) and $11.0 < \text{pH} < 12.3$ (35.2 mM β-CD). Under the conditions mentioned the polarograms are two-stage, the current of the second stage being lower than that of the first. According to the dependence of the second stage current on the height of mercury column (it is linear), this wave is adsorption-controlled and could be connected with the adsorption of an electrochemically active compound [21]. In this case calculations of the reversible half-wave potential are impossible and the results obtained are not included into Fig. 1.

The slope of the half-wave potential shift on solution pH in the case of the lowest used β-CD concentration (4.4 mM) is close to –30 mV pH^{-1} (Fig. 1), showing the participation of one β-CD anion (β-CD^-) in complex formation. Since the polarographic waves of Pb(II) reduction in the pH region under investigation are reversible, the characteristics of Pb(II) complex formation can be calculated according to Eqs. (1)–(4). The stability constant logarithm of 1:1 Pb(β-CD)$^+$ complex calculated from polarographic data in the pH range from 11.0 to 12.0 is 16.7 ± 0.2.

With the increase in β-CD concentration the same trend is observed, but the half-wave potential shift is *ca.* (–44)–(–50) mV pH^{-1} (Fig. 1), showing an additional complex formation with the predominance of the above-mentioned 1:1 Pb(β-CD)$^+$ complex. The additional Pb(II) complexes formed could be these containing two β-CD anions and/or one β-CD anion and one OH^- group. More exact calculations are impossible due to the limited pH region of Pb(II)–β-CD complex formation. Assuming that the Pb(β-CD)$^+$ complex predominates at all β-CD concentrations used, the calculations of its stability constant logarithm gave the mean value of *ca.* 16, which is in satisfactory agreement with the value obtained at the lowest β-CD concentration used.

It must be noted that unlooked-for results were obtained when increasing the β-CD concentration. In the conventional case of complex formation the half-wave potential should shift to more negative values with an increase in ligand concentration at the same pH value. In our experiments the half-wave potential does not depend on β-CD concentration. One of the possible reasons might be encapsulation of the part of lead(II) existing in the solution into the β-CD cavity which initially contains water molecules, and formation of inclusion complexes. On the one hand, the stability of the β-CD inclusion complexes is rather weak (the logarithm of equilibrium constant is less than 2) [1, 2], on the other hand the additionally performed experiments in acid Pb(II)–β-CD solutions (pH 4.0) showed no evidence of encapsulation of hydrated Pb(II) ions into β-CD cavity or formation of an other kind of complex – the half-wave potential and limiting current values remained almost constant with increasing the β-CD concentration from 0 to 12.5 mM. Thus, encapsulation of part of lead(II) existing in alkaline solutions into the β-CD cavity is seemingly little presumable. The eventual reason of independence of Pb(II) complexation with increase in β-CD concentration could be micellization of β-CD and exceeding of critical micelle concentration [22], *i. e.* formation of high molecular mass β-CD associates which do not participate in complex formation, the concentration of unassociate part of β-CD being constant.

The results of β-CD complex formation with Pb(II) were confirmed by UV-spectrophotometry. The Pb(β-CD)$^+$ complex compound has a distinct absorption maximum at 260 nm with the molar extinction coefficient (ε) value equal to 5500 mol^{-1} l cm^{-1} (Fig. 3, curve 1). It must be noted that absorbance of alkaline β-CD solutions and solutions of sodium hydroxide at 230–300 nm is negligible (less than 0.02) and does not interfere with the measurements.

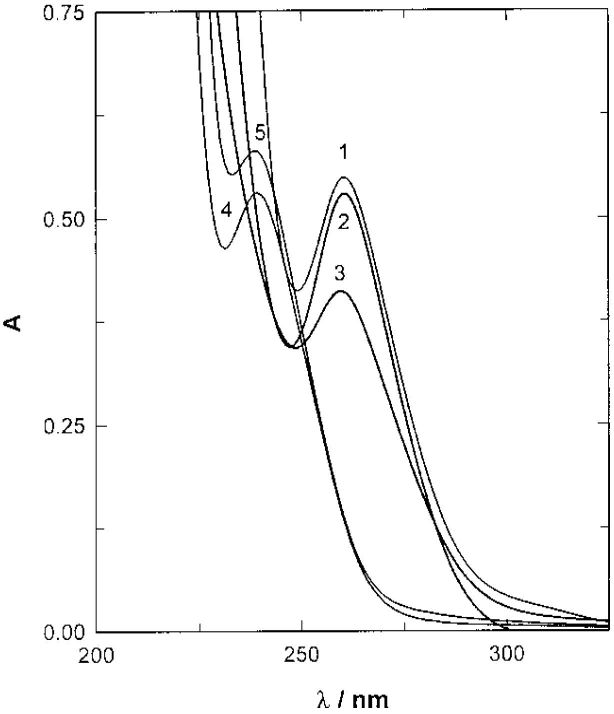

Fig. 3. Pb(II) UV-spectra in alkaline solutions of β-cyclodextrin. Solution composition (mM): $[\text{Pb(II)}]_0$ – 0.1; $[\beta\text{-cyclodextrin}]_0$ – 0.1. Solution pH: 1 – 11.0, 2 – 11.5, 3 – 12.0, 4 – 13.0, 5 – 14.0. 20 °C

The calculated concentration of the uncomplexed ("free") Pb^{2+} ions in the solutions under investigation at pH 9.7–11.3 is rather low and reaches 10^{-14}–10^{-17} M depending on β-CD concentration and solution pH (Fig. 4).

Quite unexpected results were obtained with solutions of higher alkalinity (pH > 11.5), namely,

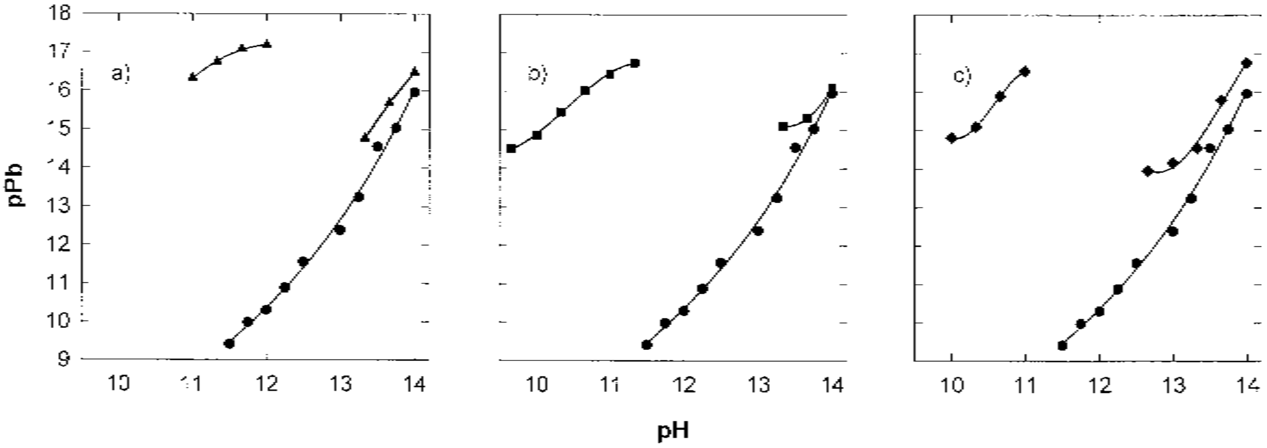

Fig. 4. Dependence of pPb on solution pH calculated from the polarographic data. Solution composition (mM): $[\text{Pb(II)}]_0$ – 0.5; $[\beta\text{-cyclodextrin}]_0$: ▲ – 4.4, ■ – 22.0, ◆ – 35.2, ● – 0; J = 1; 20 °C

$-\Delta E_{1/2}$ values began decreasing with the increase of pH. The opposite behaviour of $\Delta E_{1/2}$ could be expected for the Pb(β-CD)$^+$ complex – according to β-CD deprotonization constant value (pK_a = = 12.2 [16, 17]), in the case of 1:1 complex formation the half-wave potential of Pb(II) reduction should shift to more negative values by *ca.* 23 mV when pH rises from 11 to 12, and by 12 mV when pH increases from 12 to 13. With a further increase in solution pH the half-wave potential should remain practically constant due to full deprotonization of β-CD. The more positive value of $\Delta E_{1/2}$ is indicative of a higher concentration of free Pb^{2+} ions, *i. e.* a lower complexation of Pb(II) (Fig. 4).

With the aim to clear up other possible equilibria in the system under investigation, additional experiments were carried out in the absence of β-CD. In alkaline solutions of Pb(II) the slope of the dependence of half-wave potential shift on solution pH is ~ –60 mV pH^{-1} in the pH range from 11.5 to 12.5 and ~ –90 mV pH^{-1} at pH from 13 to 14 (Fig. 5, curve 2) showing formation of two kinds of Pb(II) hydroxy-species. The data are in accordance with the existence of the complexes $Pb(OH)_2$ (see below) and $Pb(OH)^-_3$, the stability constant logarithms being 11.3 ± 0.2 and 12.5 ± 0.2, respectively. These values are in agreement with that obtained previously by other investigators [23–27], except [28], where the stability constant values are *ca.* three orders of magnitude lower – apparently due to the influence of a high concentration of Cl$^-$ ions contained in the background electrolyte. Interestingly, no evidence of polynuclear lead(II) hydroxy-species formation was observed, *i. e.* the Pb(II) reduction half-wave potential practically did not depend on Pb(II) concentration (*cf.* curves 1 and 2 in Fig. 5).

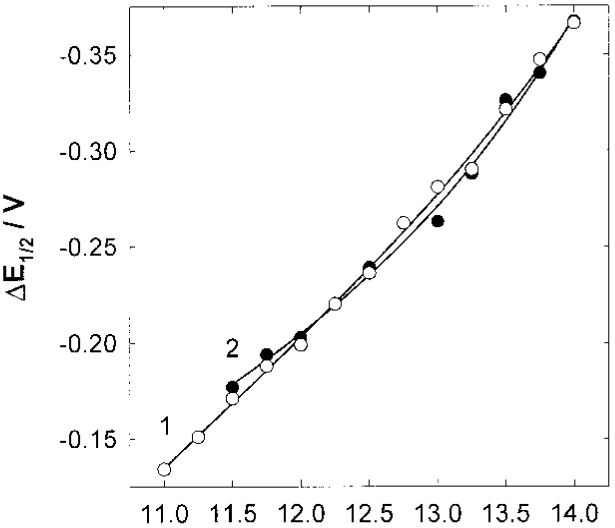

Fig. 5. Dependence of Pb(II) reduction half–wave potential shift ($\Delta E_{1/2}$) on solution pH in sodium hydroxide solutions. $[Pb(II)]_0$ (mM): 1 – 0.1, 2 – 0.5; J = 1; 20 °C

Speaking about a soluble $Pb(OH)_2$ complex, the structure of this complex must be different from that of $Pb(OH)_2$ precipitate. Since there are data to confirm existence of Pb(II) hydroxy-cation (PbOH)$^+$ [29], the possible structure of the soluble $Pb(OH)_2$ complex could be [Pb(OH)](OH), *i. e.* containing one OH$^-$ group in the first coordination sphere and one OH$^-$ group in the second coordination sphere. The data about the existence of soluble $Pb(OH)_2$ complex compound are given in [24, 26, 27].

Assuming that only a $Pb(OH)^-_3$ complex exists in the solution, the calculations show that the precipitate should form at pH < 12.3 (Fig. 6). Our experiments show that no precipitation is observed at pH 11.5–14.0, *i. e.* an additional complex compound should form under the conditions investigated. The calculations performed assuming that both hydroxy-complexes (soluble $Pb(OH)_2$ and $Pb(OH)^-_3$) exist in the pH region studied are in agreement with experimental data (Fig. 6).

Calculations of lead(II) ions distribution among the complexes in sodium hydroxide solutions sho-

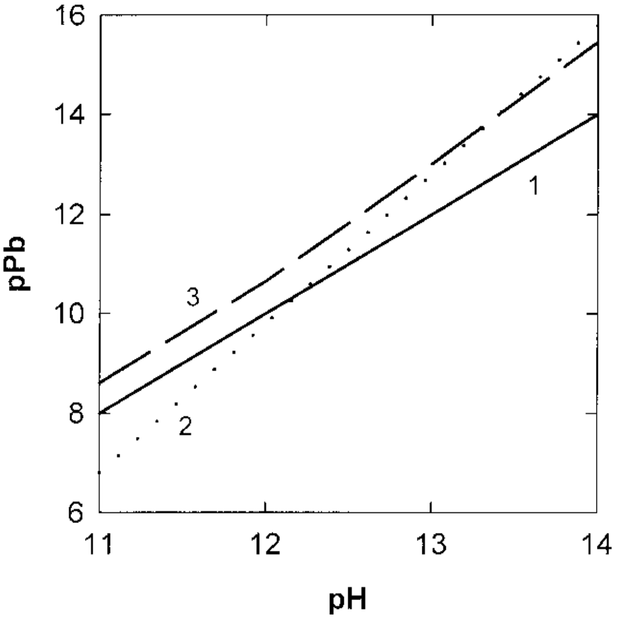

Fig. 6. Dependence of pPb on solution pH. $[Pb(II)]_0$– 0.5 mM. The solid line represents precipitation of $Pb(OH)_2$ (K_{S0} = 10^{-14}). The dotted line reseprents results of calculations in the presence of $Pb(OH)^-_3$ complex alone ($\log\beta_{Pb(OH)^-_3}$ = 12.5). The dashed line reseprents results of calculations in the presence of both $Pb(OH)_2$ ($\log\beta_{Pb(OH)_2}$ = 11.3) and $Pb(OH)^-_3$ complexes ($\log\beta_{Pb(OH)^-_3}$ = 12.5)

wed that at pH 11–12.5 the soluble complex $Pb(OH)_2$ predominates. With rising pH it converts to $Pb(OH)_3^-$, which predominates at pH over 13 (Fig. 7).

Formation of different kinds of Pb(II) hydroxy-complexes in sodium hydroxide solutions was confirmed by UV-spectrophotometry (Fig. 8). Assuming that at the lower pH limit (pH 11.25) $Pb(OH)_2$ complex and at the higher pH limit (pH 14.0) $Pb(OH)_3^-$ predominates, the molar extinction coefficients of these complexes were calculated: $\varepsilon_{Pb(OH)_2}$ = = 4300 mol^{-1} l cm^{-1} and $\varepsilon_{Pb(OH)_3^-}$ = 6000 mol^{-1} l cm^{-1} (λ_{max} = 238 nm). The pH-dependent changes in spectra (Fig. 6) correlated well with a lead(II) distribution diagram among the hydroxy-species.

After explanation of the processes taking place in the system Pb(II) – OH^- ions, we can revert to the results obtained in alkaline Pb(II)–β-CD system. When comparing changes in the spectra of the Pb(II)–β-CD system with an increase in solution pH (Fig. 3) with that of system Pb(II) – OH^- ions (Fig. 8) one can see a clear evidence of the decomposition of $Pb(\beta\text{-CD})^+$ complex and its transformation to $Pb(OH)_2$ and $Pb(OH)_3^-$ hydroxy-complexes at pH over 11.5 – the absorption of $Pb(\beta\text{-CD})^+$ complex at 260 nm decreases in the pH range 11.5–12.0 with a further shift of the absorption maximum to a shorter wavelength and a rise of absorption maximum at 238 nm in the pH region from 13.0 to 14.0. Actually, the wavelength 238 nm is characteristic of lead(II) hydroxy-species (Fig. 8). A comparison of spectra at pH 14 in the presence and in the absence of β-CD (*cf.* curve 5 in Fig. 3 and curve 12 in Fig. 8) shows that the spectra approximately coincide. Thus we can state an almost full conversion of $Pb(\beta\text{-CD})^+$ complex into $Pb(OH)^-_3$ hydroxy-complex at the above-mentioned pH value.

Figure 1 presents an additional evidence of $Pb(\beta\text{-CD})^+$ complex conversion to $Pb(OH)_3^-$ hydroxy-complex at pH over 13 – the values of $\Delta E_{1/2}$ of Pb(II) reduction in the presence of β-CD are only slightly more negative than in the absence of β-CD when the $Pb(OH)^-_3$ complex predominates in solution. The values of the limiting current also confirm changes in the lead(II) complex formation – the values of Pb(II) reduction limiting current in alkaline β-CD containing solutions remain almost constant up to pH ca. 11.5; with a further increase in solution pH the limiting current values rise and approach that obtained in the absence of β-CD (Table 1).

The diffusion coefficient values of different Pb(II) species were calculated from polarografic data, showing a large-size complex species formation in alkaline solutions containing β-CD (Table 2).

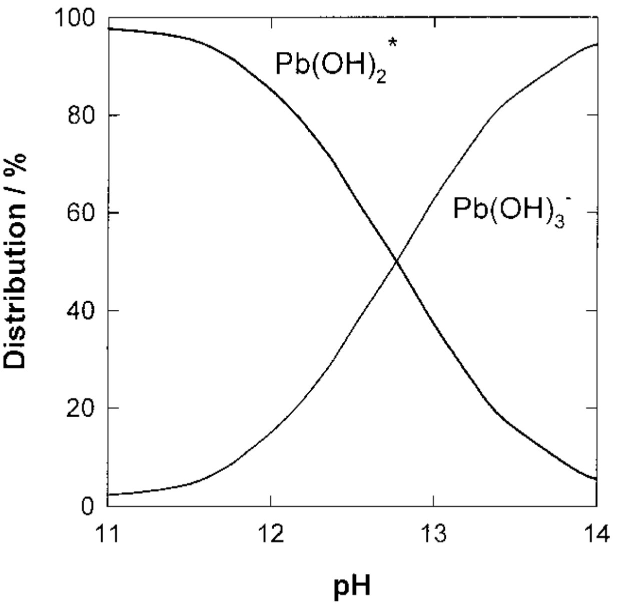

Fig. 7. Distribution diagram of Pb(II) species in sodium hydroxide solution calculated according to the polarographic data. $[Pb(II)]_0$ – 0.5 mM; $\log\beta_{Pb(OH)_2}$ = 11.3; $\log\beta_{Pb(OH)_3^-}$ = 12.5

* $Pb(OH)_2$ is soluble complex compound with the structure different from that of $Pb(OH)_2$ precipitate.

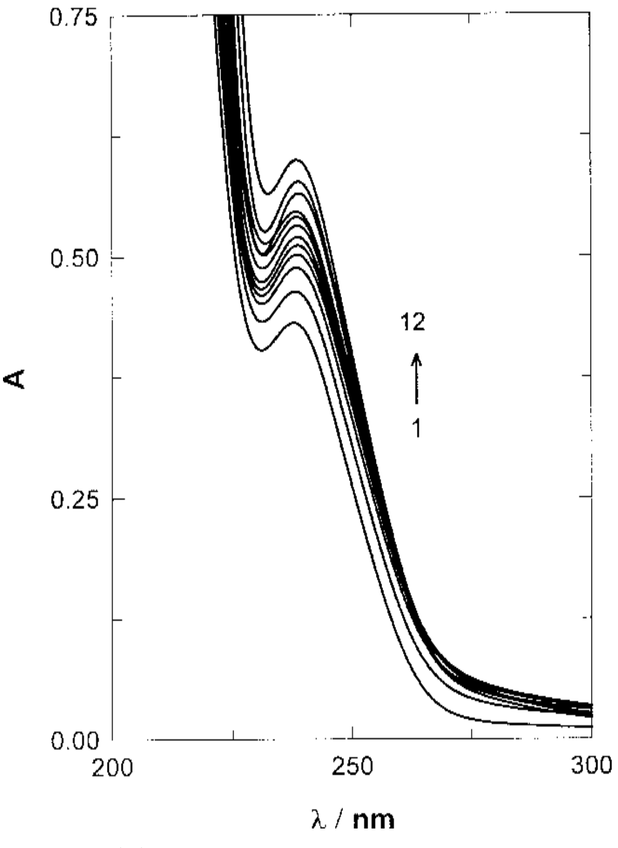

Fig. 8. Pb(II) UV–spectra in solutions of sodium hydroxide. Solution composition (mM): $[Pb(II)]_0$ – 0.1. Solution pH: 1 – 11.25, 2 – 11.50, 3 – 11.75, 4 – 12.00, 5 – 12.25, 6 – 12.50, 7 – 12.75, 8 – 13.00, 9 – 13.25, 10 – 13.50, 11 – 13.75, 12 – 14.00. 20 °C.

Table 2. **Diffusion coefficient values of Pb(II) species calculated from polarographic data ($[Pb(II)]_0$ = 0.5 mM; J = 1.0; 20 °C)**

Ligand	Pb(II) complex compound	Solution pH	D × 10^6, cm^2 s^{-1}
Without ligands	Hydrated Pb(II) ions	4.0	9.8
OH^- ions	Soluble $Pb(OH)_2$	11.5–12.0	6.8
	$Pb(OH)^-_3$	13.3–14.0	13.0
β-CD	$Pb(β\text{-}CD)^+$	11.0–11.7 (4.4 mM β-CD)	2.2
	$Pb(β\text{-}CD)^+$	9.7–11.0 (22.0 mM β-CD)	1.7
	$Pb(β\text{-}CD)^+$	10.0–11.0 (35.2 mM β-CD)	1.2

A decrease in Pb(II) ions complexation and transformation of the $Pb(β\text{-}CD)^+$ complex to $Pb(OH)^-_3$ at higher pH is seemingly connected with a decrease in the activity of β-CD anion in strongly alkaline solutions, especially as a decrease in the activity of ligands in strongly alkaline solutions was observed earlier [30–32]. This decrease in activity might be attributed to an additional association of β-CD anions in alkaline solutions, whereas β-CD associates are known in crystal form when crystallizing β-CD from a hot saturated solution [33].

Finally, it should be noted that there is no evidence to suggest that $Pb(OH)^-_3$ encapsulates into the β-CD cavity.

CONCLUSIONS

1. Undissociated β-CD does not interact with Pb(II) ions, but the deprotonated β-CD participates in complex formation with Pb(II) ions. Lead(II) reacts with the β-cyclodextrin anion in alkaline solutions ($9.7 < pH < 12.0$) forming presumably a 1:1 complex with the stability constant logarithm value equal to 16.7 ± 0.2 (20 °C, ionic strength 1.0, 4.4 mM β-cyclodextrin, $11.0 < pH < 12.0$) and the molar extinction coefficient value *ca.* 5500 (λ_{max} = 260 nm).
2. The diffusion coefficient values of Pb–β-cyclodextrin complex are in the range (2.2–1.2) × $\times 10^{-6}$ cm^2 s^{-1}, depending on β-cyclodextrin concentration.
3. At pH over 11.5–12.0, the Pb–β-cyclodextrin complex decomposes and converts to Pb(II) hydroxycomplexes. This process occurs with a decrease in Pb(II) complexation degree, seemingly due to a decrease in β-cyclodextrin anion activity.
4. No evidence of $Pb(OH)^-_3$ encapsulation into the β-CD cavity (host–guest complex formation) was found.

ACKNOWLEDGEMENTS

Authors are most thankful to Prof. A. Vaškelis for helpful discussion.

This work was partly reported at the *11th European Carbohydrate Symposium* (Lisbon – Portugal, 2001). GG thanks Lithuanian Commission for International Studies for travel grant.

Received 18 October 2001
Accepted 29 November 2001

References

1. K. A. Connors, *Chem. Rev.*, **97**, 1325 (1997).
2. M. V. Rekharsky and Y. Inoue, *Chem. Rev.*, **98**, 1875 (1998).
3. Y. Matsui, T. Kurita, and Y. Date, *Bull. Chem. Soc. Japan*, **45**, 3229 (1972).
4. Y. Matsui, T. Kurita, M. Yagi, T. Okayama, K. Mochida, and Y. Date, *Bull. Chem. Soc. Japan*, **48**, 2187 (1975).
5. K. Mochida and Y. Matsui, *Chem. Lett.*, 963 (1976).
6. Y. Matsui and K. Kinugawa, *Bull. Chem. Soc. Japan*, **58**, 2981 (1985).
7. R. Fuchs, N. Habermann and P. Klüfers, *Angew. Chem. Int. Ed.* **105**, 895 (1993).
8. P. K. Bose and P. L. Polavarapu, *Carbohydr. Res.*, **323**, 63 (2000).
9. B. U. Nair and G. C. Dismukes, *J. Am. Chem. Soc.*, **105**, 124 (1983).
10. N. R. Russel and M. McNamara, *J. Incl. Phen. Molec. Recogn. Chem.*, **7**, 455 (1989).
11. M. McNamara and N. R. Russel, *J. Incl. Phen. Molec. Recogn. Chem.*, **10**, 485 (1991).
12. G. Grincienė, E. Norkus and R. Vaitkus, *11th European Carbohydrate Symposium. Book of Abstracts*, Lisboa–Portugal, 305 (2001).
13. J. Heyrovsky and J. Kuta, *Principles of Polarography*, Academic Press, New York, 1966.
14. E. Norkus and A. Vaškelis, *Electroanalysis*, **8**, 171 (1996).
15. *Stability Constants of Metal-Ion Complexes. Special Publication No 17*, Supplement No 1, eds. L. G. Sillen and A. E. Martell, Chemical Society, London, 1964.
16. S. Li and W. C. Purdy, *Chem. Rev.*, **92**, 1457 (1992).
17. J. Szejtli, *Chem. Rev.*, **98**, 1743 (1998).
18. E. Norkus, A. Vaškelis and J. Reklaitis, *Koord. Khim.*, **14**, 325 (1988).

19. E. Norkus, A. Vaškelis, R. Vaitkus and J. Reklaitis, *J. Inorg. Biochem.*, **60**, 299 (1995).
20. E. S. Lygin and S. Z. Ivanov, *Sakh. Prom.*, **41**, 23 (1967).
21. A. M. Bond, *Modern Polarographic Methods in Analytical Chemistry*, Marcel Dekker, New York, 1980.
22. K. L. Mittal, *Micellization, Solubilization and Microemulsions*, Plenum Press, New York, 1977.
23. J. Heyrovsky, *Trans. Faraday Soc.*, **19**, 692 (1923).
24. J. Inczedy, *Analytical Applications of Complex Equilibria*, Akademiai Kiado, Budapest, 1976.
25. A. A. Vlček, *Coll. Czech. Chem. Comm.*, **20**, 400 (1955).
26. J. W. Oliver and D. N. Hume, *Analyt. Chim. Acta*, **20**, 559 (1959).
27. B. Carell and A. Olin, *Acta Chem. Scand.*, **14**, 1999 (1960).
28. G. Schorsch and N. Inguri, *Acta Chem. Scand.*, **21**, 2727 (1967).
29. P. Ripan and I. Ceteanu, *Chemistry of Metals*, Mir, Moscow, 1971 (in Russian).
30. E. Norkus and A. Vaškelis, *Chemija*, N 4, 19 (1995).
31. E. Norkus, A. Vaškelis and I. Žakaitė, *Talanta*, **43**, 465 (1996).
32. E. Norkus and R. Pauliukaitė, *Polish J. Chem.*, **74**, 1231 (2000).
33. W. Saenger, in *Physical Supramolecular Chemistry*, eds. L. Echegoyen and A. E. Kaifer, Kluwer Academic Publishers, Dordrecht, 1996.

E. Norkus, G. Grincienė, R. Vaitkus

PB(II) KOMPLEKSŲ SUSIDARYMAS ŠARMINIUOSE Β-CIKLODEKSTRINO TIRPALUOSE

Santrauka

Nuolatinės srovės poliarografijos ir UV spektro dalies spektrofotometrijos metodais nustatyta, kad tirpalo pH esant 9,7–12,0, švino(II) jonai su β-ciklodekstrinu sudaro kompleksinį junginį, kurio sudėtis galėtų būti $Pb(\beta\text{-}CD)^+$ (čia $\beta\text{-}CD^-$ yra β-ciklodekstrino anijonas). Šio junginio apskaičiuotoji patvarumo konstantos logaritmo vertė yra 16,7 ± ± 0,2 (20°C; joninė jėga 1,0; 4,4 mM β-ciklodekstrino; $11{,}0 < pH < 12{,}0$), o molinis absorbcijos koeficientas yra ~5500 ($\lambda_{max} = 260$ nm). Nustatytosios $Pb(\beta\text{-}CD)^+$ komplekso difuzijos koeficiento vertės yra nuo $2{,}2 \times 10^{-6}$ iki $1{,}2 \times 10^{-6}$ $cm^2\ s^{-1}$. Esant didesnėms tirpalo pH vertėms ($pH > 11{,}5$–12), $Pb(\beta\text{-}CD)^+$ kompleksas suyra ir pereina į Pb(II) hidroksikompleksus, tai aiškinama β-ciklodekstrino anijono aktyvumo sumažėjimu stipriai šarminėje terpėje. Parodyta, kad β-ciklodekstrinas nesudaro „šeimininko–svečio“ tipo įsiterpimo kompleksų su $Pb(OH)_3^-$.