ELSEVIER

Carbohydrate Research 337 (2002) 1657–1661

CARBOHYDRATE RESEARCH

www.elsevier.com/locate/carres

Interaction of lead(II) with β-cyclodextrin in alkaline solutions

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

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

Received 25 October 2001; accepted 6 February 2002

Abstract

Polarographic and UV-spectrophotometric investigations of Pb(II) complex formation with β-cyclodextrin have showed that the complexation of Pb(II) ions begins at pH >10. The formation of lead(II) 1:1 complex with the β-cyclodextrin anion was observed at pH 10–11.5. The logarithm of the stability constant of this complex compound is 15.9 ± 0.3 (20 °C, ionic strength 1.0), and the molar extinction coefficient value is ca. 5500 ($\lambda_{max} = 260$ nm). With further increase in solution pH the Pb–β-cyclodextrin complex decomposes and converts to $Pb(OH)_2$ or $Pb(OH)_3^-$ 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. Neither $Pb(OH)_2$ nor $Pb(OH)_3^-$ encapsulation into β-CD cavity was observed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: β-Cyclodextrin; Lead(II); Complex formation

1. Introduction

Cyclodextrins (CD) inclusion complex formation with different compounds is well known and investigated.[1,2] On the contrary, information about cyclodextrin interaction with heavy metal ions in aqueous solutions is not numerous. Cu(II) complexes with CD are the most investigated. The data about 2:1, 1:1 and 2:2 Cu(II)–β-CD complex compounds are given in Refs. 3–8.

The complexation of other metal ions with CD has been investigated less. A 2:1 Mn(III)–β-CD complex was reported in Refs. 9 and 10. The synthesis and characterization of 2:1 Cr(III), Co(II), Cu(II), and Ni(II) complexes with β-cyclodextrin are described in Ref. 11. It must be noted that the data obtained are only qualitative and do not provide information about stability of the complexes in aqueous solutions.

Since the preliminary results show 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 β-cyclodextrin complexing ability in alkaline solutions.

2. 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 the ionic strength (J) of the solutions constant and equal in polarographic experiments (1 M).

dc 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^{-1}. 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 satd 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 (Table 1):[13]

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

---

* Corresponding author. Tel.: +370-2-611731; fax: +370-2-617018.
E-mail address: norkus@ktl.mii.lt (E. Norkus).

0008-6215/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0008-6215(02)00044-7

Table 1
Diffusion coefficient values of Pb(II) species calculated from polarographic data

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

$[Pb(II)]_0 = 0.5$ mM; $J = 1.0$; 20 °C.

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}), and 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 $\log(\bar{i}/\bar{i}_{\mathrm{lim}} - \bar{i})$ against E.

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

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

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

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

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 $\Delta E_{1/2}$:

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

where $[Pb(II)]_0$ is the total Pb(II) concentration.

UV-spectrophotometry.—The UV-spectra were recorded using a Perkin–Elmer Lambda 35 UV–Vis spectrometer at 20 °C in 1 cm-thick quartz cells. Water was the comparison solution.

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

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

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

pH-metric measurements.—Measurements of the solution pH were carried out using a Toledo Mettler MP 220 pH-meter.

3. 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 $Pb(OH)_2$ solubility product given in Ref. 14—they are in the range 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. In the pH range 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 deprotonation of β-CD in alkaline solutions (pK_a 12.2[15,16]) and herewith to strengthening of β-CD complexing ability and complex formation. Thus it can be concluded, 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, i.e. saccharose,[17,18] having a similar value of the deprotonation constant, equal to 12.43.[19].

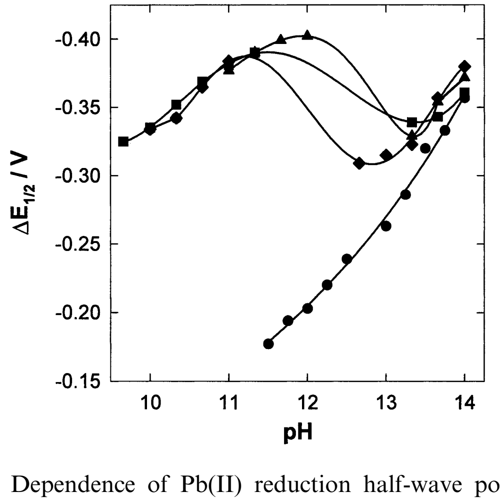

Fig. 1. Dependence of Pb(II) reduction half-wave potential shift ($\Delta E_{1/2}$) on solution pH. Solution composition (mM): $[Pb(II)]_0$, 0.5; [β-cyclodextrin]$_0$: (▲) 4.4; (■) 22.0; (◆) 35.2; (●) 0; $J = 1$; 20 °C.

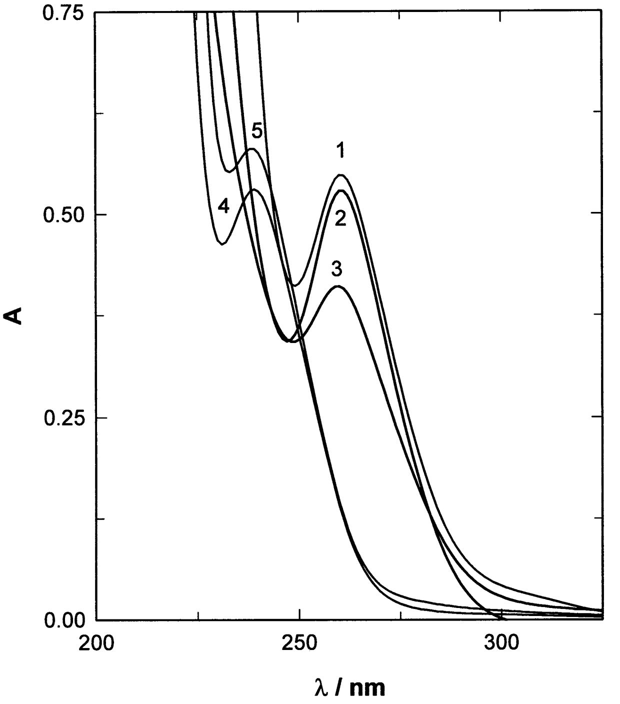

Fig. 2. Pb(II) UV-spectra in alkaline solutions of β-cyclodextrin. Solution composition (mM): $[\mathrm{Pb(II)}]_0$, 0.1; $[\beta\text{-cyclodextrin}]_0$, 0.1. Solution pH: (1) 11.0; (2) 11.5; (3) 12.0; (4) 13.0; (5) 14.0; 20 °C.

The slope of the half-wave potential shift on solution pH is ~ -30 mV pH^{-1} (Fig. 1) showing participation of one β-CD anion (β-CD^{-}) in complex formation.

According to the experimental data, the Pb(II)–β-CD complex is formed only in solutions of medium alkalinity (pH ca. 9.7–11.3). Whereas unsubstituted β-CD is a rather weak acid (pK_a 12.2[15,16]), we presume that at pH values mentioned, the deprotonization of exclusively one secondary OH-group of β-CD occurs. Since only deprotonated OH-groups of carbohydrates or polyols form strong enough complexes with metal ions,[20,21] formation of 1:1 Pb(II)–β-CD complex is suggested. There is also the theoretical possibility of 1:2 Pb(II)–β-CD complex formation, but our experimental results ($\Delta E_{1/2}$ dependence on pH) do not confirm this assumption. On the other hand, e.g., 2:2 Cu(II)–β-CD complex formation is also justified.[7] In the latter case, each Cu(II) ion is bound to two deprotonized OH-groups of either β-CD unit. Such a structure is possible in strongly alkaline solutions, when the deprotonization of several OH-groups could be expected. Our preliminary results of polarographic investigations showed, that complexation of Cu(II) ions with β-CD begins at pH 11.7–12.0, i.e., at higher pH then that of Pb(II) ions. Thus, in our opinion, 1:1 Pb(II)–β-CD complex formation in medium alkaline solutions is reasonable, taking into account the large excess of β-CD in the solutions under investigation.

Since the polarographic waves of Pb(II) reduction in the system under the 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 $\mathrm{Pb}(\beta\text{-CD})^{+}$ complex calculated from polarographic data in the pH range from 9.7 to 11.3 is equal to 15.9 ± 0.3. The results of the polarographic investigations were confirmed by UV-spectrophotometry. The $\mathrm{Pb}(\beta\text{-CD})^{+}$ complex has a distinct absorption maximum at 260 nm with the molar extinction coefficient (ε) value equal to 5500 mol^{-1} L cm^{-1} (Fig. 2, 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. With respects to the possible structure of $\mathrm{Pb}(\beta\text{-CD})^{+}$ complex, we presume that the partly hydrated Pb(II) ion is bound to the deprotonated secondary OH-group, which is located in the larger rim of the β-CD torus and is more acidic than the primary one. We expect that there is any additional Pb(II) complexation in the β-CD cavity. The calculated concentration of the uncomplexed ('free') Pb^{2+} ions in the solutions under investigation at pH

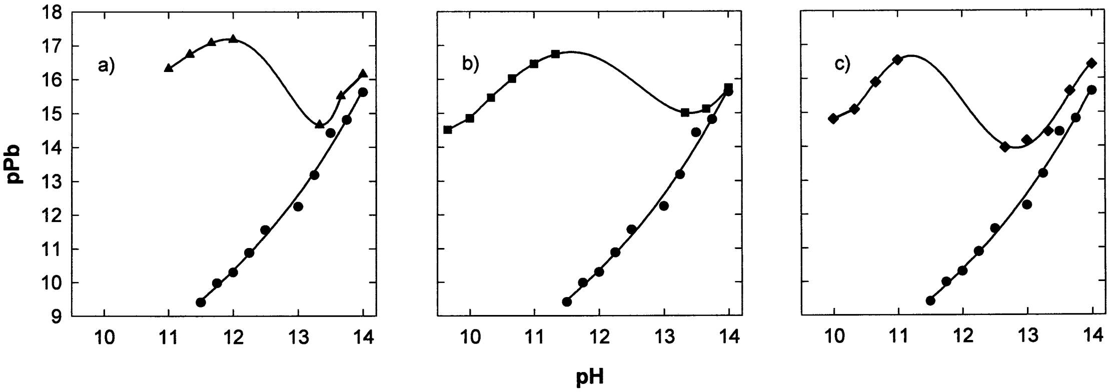

Fig. 3. Dependence of pPb on solution pH calculated from the polarographic data. Solution composition (mM): $[\mathrm{Pb(II)}]_0$, 0.5; $[\beta\text{-cyclodextrin}]_0$: (▲) 4.4; (■) 22.0; (◆) 35.2; (●) 0; $J = 1$; 20 °C.

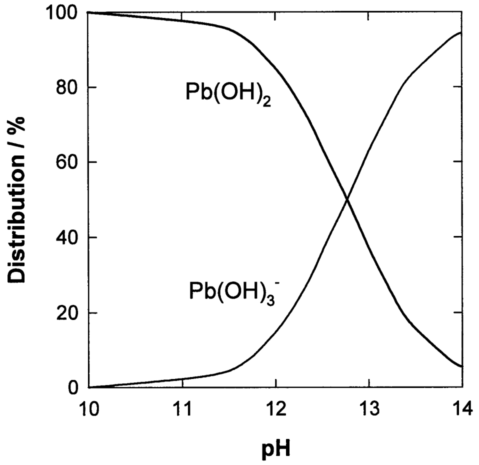

Fig. 4. Distribution diagram of Pb(II) species in sodium hydroxide solution calculated according to the polarographic data. $[\mathrm{Pb(II)}]_0$, 0.5 mM; $\log \beta_{\mathrm{Pb(OH)_2}} = 11.3$; $\log \beta_{\mathrm{Pb(OH)_3^-}} = 12.5$.

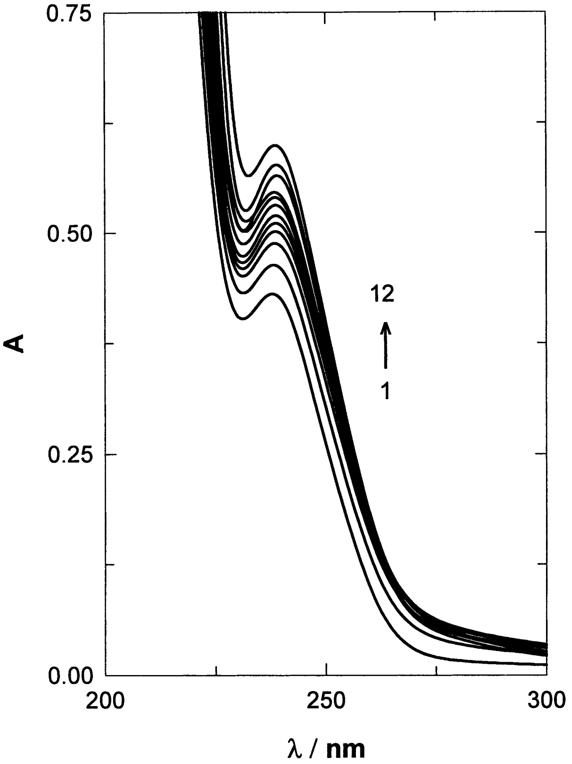

Fig. 5. Pb(II) UV-spectra in solutions of sodium hydroxide. Solution composition (mM): $[\mathrm{Pb(II)}]_0$, 0.1. Solution pH: (1) 11.25; (2) 11.50; (3) 11.75; (4) 12.00; (5) 12.25; (6) 12.50; (7) 12.75; (8) 13.00; (9) 13.25; (10) 13.50; (11) 13.75; (12) 14.00; 20 °C.

9.7–11.3 is rather low and reaches 10^{-14}–10^{-17} M depending on β-CD concentration and solution pH (Fig. 3).

Quite unexpected results were obtained with solutions of higher alkalinity (pH > 11.5), namely, $-\Delta E_{1/2}$ values began decreasing with the increase in pH. The opposite behavior of $\Delta E_{1/2}$ might be expected for the Pb(β-CD)$^+$ complex—according to β-CD deprotonization constant value (pK_a 12.2[15,16]) 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 increases 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 degree of Pb(II) ions (Fig. 3).

With the aim to investigate other possible equilibria, 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. 1, circles) showing formation of two kinds of Pb(II) hydroxy-species. The data are in accordance with the existence of the $\mathrm{Pb(OH)_2}$ and $\mathrm{Pb(OH)_3^-}$ complexes, the stability constant logarithms being 11.3 ± 0.2 and 12.5 ± 0.2, respectively. These values are in agreement with those obtained previously by other investigators,[22–26] except,[27] where the stability constants values are ca. three orders of magnitude lower—apparently due to the influence of a high concentration of $\mathrm{Cl^-}$ ions contained in the background electrolyte.

Calculations of lead(II) ions distribution among the complexes in sodium hydroxide solutions showed that the complex $\mathrm{Pb(OH)_2}$ predominates at pH 10–12.5. With rising pH, it converts to $\mathrm{Pb(OH)_3^-}$, which predominates at pH above 13 (Fig. 4). The formation of different kinds of Pb(II) hydroxy-complexes in sodium hydroxide solutions was confirmed by UV-spectrophotometry (Fig. 5). Assuming that at the lower pH limit (pH 11.25) $\mathrm{Pb(OH)_2}$ complex and at the higher pH limit (pH 14) $\mathrm{Pb(OH)_3^-}$ complex predominates, the molar extinction coefficients of these complexes were calculated: $\varepsilon_{\mathrm{Pb(OH)_2}} = 4300$ mol^{-1} L cm^{-1} and $\varepsilon_{\mathrm{Pb(OH)_3^-}} = 6000$ mol^{-1} L cm^{-1} ($\lambda_{\max} = 238$ nm). The pH-dependent changes in spectra (Fig. 5) correlate well with a lead(II) distribution among the hydroxy-species diagram (Fig. 4).

Comparison of changes in the spectra of Pb(II)–β-CD system with the increase in solution pH (Fig. 2) with that of the Pb(II)–OH$^-$ ions system (Fig. 5) gives clear evidence of the decomposition of Pb(β-CD)$^+$ complex and its transformation to $\mathrm{Pb(OH)_2}$ and $\mathrm{Pb(OH)_3^-}$ hydroxy-complexes at pH above 11.5—the absorption of Pb(β-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 an increase in absorption maximum at 238 nm in the pH region from 13.0 to 14.0, the wavelength 238 nm being characteristic of lead(II) hydroxy-species (Fig. 5). A comparison of spectra at pH 14 in the presence and in the absence of β-CD (cf. curve 5 in Fig. 2 and curve 12 in Fig. 5) shows that the spectra approximately coincide. Thus, almost complete conversion of Pb(β-CD)$^+$ complex into $Pb(OH)_3^-$ hydroxy-complex is attained at the above-mentioned pH value.

Fig. 1 presents additional evidence of Pb(β-CD)$^+$ complex conversion to $Pb(OH)_3^-$ hydroxy-complex at pH above 13—the values of $\Delta E_{1/2}$ of Pb(II) reduction in the presence of β-CD are only slightly more negative than those 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 increase and approach those obtained in the absence of β-CD.

A decrease in Pb(II) ions complexation and transformation of the Pb(β-CD)$^+$ complex into $Pb(OH)_3^-$ at higher pH is seemingly connected with a decrease in the activity of an β-CD anion in strongly alkaline solutions, especially as a decrease in the activity of ligands in strongly alkaline solutions was observed earlier.[28–30] 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.[31]

Finally, it should be noted that there is no evidence to suggest that $Pb(OH)_2$ or $Pb(OH)_3^-$ encapsulate into the β-CD cavity.

4. Conclusions

1. Lead(II) reacts with the β-cyclodextrin anion in alkaline solutions ($10 < pH < 11.5$) forming a 1:1 complex with the stability constant value equal to $10^{15.9}$ and the molar extinction coefficient value equal to 5500 ($\lambda_{max} = 260$ 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, and are ca. 3–10 times lower than those of hydrated Pb(II), $Pb(OH)_2$ or $Pb(OH)_3^-$ hydroxy-complexes.
3. At pH above 11.5, the Pb–β-cyclodextrin complex decomposes and converts to $Pb(OH)_2$ or $Pb(OH)_3^-$ hydroxy-complexes. 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 $Pb(OH)_2$ or $Pb(OH)_3^-$ encapsulation into the β-CD cavity (host–guest complex formation) was found.

Acknowledgements

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

References

1. Connors, K. A. *Chem. Rev.* **1997**, *97*, 1325.
2. Rekharsky, M. V.; Inoue, Y. *Chem. Rev.* **1998**, *98*, 1875.
3. Matsui, Y.; Kurita, T.; Date, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3229.
4. Matsui, Y.; Kurita, T.; Yagi, M.; Okayama, T.; Mochida, K.; Date, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2187.
5. Mochida, K.; Matsui, Y. *Chem. Lett.* **1976**, 963.
6. Matsui, Y.; Kinugawa, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2981.
7. Fuchs, R.; Habermann, N.; Klüfers, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 852.
8. Bose, P. K.; Polavarapu, P. L. *Carbohydr. Res.* **2000**, *323*, 63.
9. Nair, B. U.; Dismukes, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 124.
10. Russel, N. R.; McNamara, M. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1989**, *7*, 455.
11. McNamara, M.; Russel, N. R. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1991**, *10*, 485.
12. Grinciene, G.; Norkus, E.; Vaitkus, R. *11th European Carbohydrate Symposium. Book of Abstracts*; Lisbon, Portugal, 2001; p. 305.
13. Heyrovsky, J.; Kuta, J. *Principles of Polarography*; Academic Press: New York, 1966.
14. *Stability Constants of Metal-Ion Complexes. Special Publication No. 17*; Supplement No. 1; Sillen, L. G.; Martell, A. E., Eds.; Chemical Society: London, 1964.
15. Li, S.; Purdy, W. C. *Chem. Rev.* **1992**, *92*, 1457.
16. Szejtli, J. *Chem. Rev.* **1998**, *98*, 1743.
17. Norkus, E.; Vaškelis, A.; Reklaitis, J. *Koord. Khim.* **1988**, *14*, 325.
18. Norkus, E.; Vaškelis, A.; Vaitkus, R.; Reklaitis, J. *J. Inorg. Biochem.* **1995**, *60*, 299.
19. Lygin, E. S.; Ivanov, S. Z. *Sakh. Prom.* **1967**, *41*, 23.
20. Burger, K.; Nagy, L. In *Biocoordination Chemistry: Coordination Equilibria in Biologically Active Systems*; Burger, K., Ed.; Ellis Harwood: Chichester, 1990.
21. Gyurcsik, B.; Nagy, L. *Coord. Chem. Rev.* **2000**, *203*, 81.
22. Heyrovsky, J. *Trans. Faraday Soc.* **1923**, *19*, 692.
23. Chaberek, S.; Courtney, R. C.; Martell, A. E. *J. Am. Chem. Soc.* **1952**, *74*, 5057.
24. Vlček, A. A. *Coll. Czech. Chem. Commun.* **1955**, *20*, 400.
25. Oliver, J. W.; Hume, D. N. *Anal. Chim. Acta* **1959**, *20*, 559.
26. Carell, B.; Olin, A. *Acta Chem. Scand.* **1960**, *14*, 1999.
27. Schorsch, G.; Inguri, N. *Acta Chem. Scand.* **1967**, *21*, 2727.
28. Norkus, E.; Vaškelis, A. *Chemija* **1995**, *N4*, 19.
29. Norkus, E.; Vaškelis, A.; Žakaite, I. *Talanta* **1996**, *43*, 465.
30. Norkus, E.; Pauliukaitė, R. *Polish J. Chem.* **2000**, *74*, 1231.
31. Saenger, W. In *Physical Supramolecular Chemistry*; Echegooyen, L.; Kaifer, A. E., Eds.; Kluwer Academic: Dordrecht, 1996.