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# Cadmium(II)– $\beta$ -cyclodextrin complex formation in alkaline solutions

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Eugenijus Norkus<sup>1\*</sup>,  
Giedrė Grincienė<sup>1</sup>,  
Eugenijus Butkus<sup>2</sup>,  
Rimantas Vaitkus<sup>3</sup>

<sup>1</sup>*Institute of Chemistry,  
A. Goštauto 9,  
LT-2600 Vilnius, Lithuania*

<sup>2</sup>*Vilnius University,  
Faculty of Chemistry,  
Naugarduko 24,  
LT-2006, Vilnius, Lithuania*

<sup>3</sup>*Vilnius Pedagogical University,  
Studentų 39,  
LT-2034 Vilnius, Lithuania*

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Cd(II) forms the  $\text{Cd}\beta\text{-CD}(\text{OH})_2^{2-}$  hydroxy-complex with  $\beta$ -cyclodextrin anion in alkaline solutions ( $\text{pH} > 11$ ), the logarithm of the stability constant being  $10.4 \pm 0.1$  ( $20\text{ }^\circ\text{C}$ ;  $I = 1.0$ ). The value of the diffusion coefficient obtained ( $1.0 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$ ) shows a large size Cd(II) complex species formation in alkaline solutions containing  $\beta$ -CD.

**Key words:** cadmium(II),  $\beta$ -cyclodextrin, complex formation

## INTRODUCTION

Metal ion complexes with cyclodextrins have a potential as metallo-enzyme models. On the other hand, the complexes mentioned could have a wide range of applications in catalysis and molecular recognition. Unfortunately data on the interaction of unmodified  $\beta$ -cyclodextrin ( $\beta$ -CD) with heavy metal ions are not numerous.

Most thoroughly investigated are Cu(II) complexes with CD. Data on formation of 2:1, 1:1 and 4:2 (molar ratio) Cu(II)– $\beta$ -CD complex compounds are documented [1–7].

The complexation of other metal ions with CD has been less investigated. A Mn(III)– $\beta$ -CD 2:1 complex was reported [8, 9]. The synthesis and characterization of 2:1 Cr(III), Co(II), Cu(II) and Ni(II) complexes with  $\beta$ -cyclodextrin were described [10]. The data on a mixed Co(III) complex formulated as  $[\text{Co}(\text{en})_2\text{CD}]\text{ClO}_4$  for  $\alpha$ - and  $\beta$ -CD were reported [11].

A recent publication containing quantitative data on Pb(II) complex formation with  $\beta$ -CD has shown that the complexation of Pb(II) ions starts at  $\text{pH} > 10$ . Formation of the lead(II) 1:1 complex with

the  $\beta$ -CD anion was observed at  $\text{pH} 10\text{--}11.5$ . The logarithm of the stability constant of this complex compound is  $15.9 \pm 0.3$  ( $20\text{ }^\circ\text{C}$ , ionic strength 1.0) and the molar extinction coefficient value is *ca.* 5500 ( $\lambda_{\text{max}} = 260\text{ nm}$ ) [12].

Membrane gels obtained by chemical grafting of cyclodextrins on polymethylhydrosiloxane or by incorporating into plasticized polyvinylchloride were used as heavy metal ion sensors [13]. The Nernstian responses of a membrane to Cd(II) ion and of  $\beta$ -CD to Pb(II) ion were observed.

Similar results were obtained when CD-polysiloxane gel matrices were used [14, 15]. Membranes containing  $\alpha$ -CD showed a good affinity to Cd(II) ions (28 mV / pCd), whereas membranes with  $\beta$ -CD were sensitive to Pb(II) ions.

The kinetics of the electrochemical reactions in the systems Cu(II) / Cu(Hg) and Cd(II) / Cd(Hg) in the presence of  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins were investigated by the polarography and chronocoulometric methods [16].

It should be noted that most of the data obtained are only qualitative and do not provide information on the stability of the complexes in aqueous solutions. Therefore the aim of the current work was investigation of Cd(II) complex formation equilibria in alkaline solutions of  $\beta$ -CD by means of d.c. polarography.

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\*Author for correspondence. E-mail: Norkus@ktl.mii.lt

## EXPERIMENTAL

The investigations were carried out by means of d.c.-polarography at 20 °C maintaining the ionic strength constant ( $I = 1.0 \text{ M}$ ;  $\text{NaNO}_3$ ). Analytical grade chemicals were used and  $\beta$ -cyclodextrin ( $M_r = 1135$ ) was "purum" from Fluka. The apparatus and methods have been described previously in [17] and elsewhere [18–21].

## RESULTS AND DISCUSSION

$\beta$ -CD in basic solutions dramatically enhances the solubility of Cd(II) ions, which are otherwise practically insoluble due to the formation of hydroxide gels. No Cd(II)– $\beta$ -CD complex formation is observed at  $\text{pH} < 11$ , even if there is an excess of  $\beta$ -CD in the solution. Formation of the  $\text{Cd}(\text{OH})_2$  precipitate is visually observed in the solution at  $\text{pH} 8$ – $11$ , and there is actually no polarographic wave of Cd(II) reduction.

The reversible Cd(II) reduction waves are observed at a higher pH. The polarographic waves of Cd(II) reduction in alkaline  $\beta$ -CD solutions shift to more negative potentials in the pH range from 12.0 to *ca.* 14.0 (Figure). This fact can be attributed to deprotonation the  $\beta$ -CD in alkaline solutions [22, 23] and herewith to strengthening of  $\beta$ -CD complexing ability and complex formation. Thus, it can be concluded that undissociated  $\beta$ -CD does not interact with Cd(II) ions, but the deprotonated  $\beta$ -CD participates in complex formation with Cd(II) ions. The same tendency of complex formation only, in alkaline solutions, was observed when investigating the interaction of  $\beta$ -CD with Pb(II) [12], Cu(II) [24] or, *e. g.*, studying Cu(II) complex formation with related polyhydroxylic compounds, such as saccharose [25, 26], glycerol [26, 27], D-mannitol [28] and D-sorbitol [29].

The slope of the half-wave potential shift ( $\Delta E_{1/2}$ ) depends on the solution pH and to a lesser degree on the concentration of  $\beta$ -CD (Figure). At constant concentrations of  $\beta$ -CD (0.025 and 0.04 M) the slope of the  $\Delta E_{1/2}$  dependences is equal to *ca.* 80–90 mV per pH unit, which for the single-

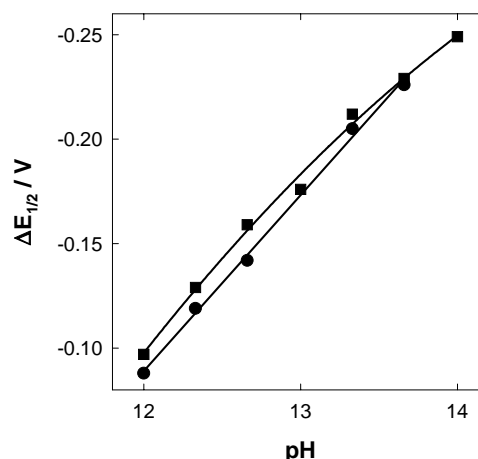


Figure. Dependence of Cd(II) reduction half-wave potential shift ( $\Delta E_{1/2}$ ) on solution pH. Solution composition (M):  $[\text{Cd}(\text{II})]_0 = 0.0005$ ;  $[\beta\text{-cyclodextrin}]_0$ : ● – 0.025, ■ – 0.040;  $I = 1$  ( $\text{NaNO}_3$ ); 20 °C

stage two electron reduction of Cd(II) indicates coordination of Cd(II) with 3 ligand particles (presumably with the anion of  $\beta$ -CD and  $\text{OH}^-$  ions). Since with increase in solution pH the activity of  $\text{OH}^-$  ions as well as the equilibrium concentration of the double-deprotonated form of  $\beta$ -CD [30] ( $\text{p}K_{\text{a}1,2} \sim 13.5$ ) rises, the number of deprotonated  $\beta$ -CD particles involved in complex formation can be determined from the dependence of  $\Delta E_{1/2}$  on  $\beta$ -CD concentration at constant pH values. The mean values of the slopes equal to *ca.* 20 mV were obtained with the fivefold increase in the concentration of  $\beta$ -CD (from 0.005 to 0.025 M), indicating that one anion of  $\beta$ -CD was taking part in the complex formation. Thus, the results obtained showed the possibility of the existence of a Cd(II) complex with two ligands – the anion of  $\beta$ -CD

Table. Data on Cd(II) interaction with  $\beta$ -cyclodextrin ( $\beta$ -CD) in alkaline solutions (0.0005 M Cd(II),  $I = 1.0$  ( $\text{NaNO}_3$ ), 20 °C)

$[\beta\text{-CD}]_0 / \text{M}$	pH	$\Delta E_{1/2} / \text{V}$ (experimental)	$\log \alpha_{\text{OH}^-}$	$\log [\beta\text{-CD}^{2-}]$	$\log \beta_{\text{Cd}\beta\text{-CD}(\text{OH})_2^{2-}}$	$\Delta E_{1/2} / \text{V}$ (calculated)
0.025	12.00	-0.088	-2.07	-3.12	10.3	-0.090
	12.33	-0.119	-1.74	-2.81	10.4	-0.122
	12.66	-0.142	-1.41	-2.51	10.2	-0.148
	13.33	-0.205	-0.74	-2.00	10.5	-0.203
	13.66	-0.226	-0.41	-1.84	10.5	-0.223
0.040	12.00	-0.097	-2.07	-2.92	10.3	-0.096
	12.33	-0.129	-1.74	-2.64	10.5	-0.122
	12.66	-0.159	-1.41	-2.31	10.6	-0.154
	13.00	-0.176	-1.07	-2.03	10.2	-0.180
	13.33	-0.212	-0.74	-1.78	10.6	-0.209
	13.66	-0.229	-0.41	-1.64	10.4	-0.232
	14.00	-0.249	-0.07	-1.53	10.3	-0.252
Mean value:						
10.4 ± 0.1						

(according to NMR results, in the case of the excess of the ligand we suggest participation of the doubly deprotonated anion  $\beta$ -CD<sup>2-</sup>, the  $pK_{a1,2}$  value being ca. 13.5 [30]) and OH<sup>-</sup> groups – with the general formula Cd $\beta$ -CD(OH)<sub>2</sub><sup>2-</sup>.

Since the polarographic waves of Cd(II) reduction in the pH region under investigation are reversible, the characteristics of Cd(II) complex formation can be calculated according to the procedures given in [17–21]. The results of the Cd $\beta$ -CD(OH)<sub>2</sub><sup>2-</sup> complex stability constant calculations correlate well (the difference between the experimental and the calculated  $\Delta E_{1/2}$  values do not exceed 7 mV), the mean value of the logarithm of the stability constant being  $10.4 \pm 0.1$  (Table).

The diffusion coefficient of the Cd(II) complex was calculated from limiting current values according to the Ilkovič equation. The value obtained ( $D = 1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) shows a *large-size* Cd(II) complex species formation in alkaline solutions containing  $\beta$ -CD. It could be noted that the Cd $\beta$ -CD(OH)<sub>2</sub><sup>2-</sup> diffusion coefficient value obtained is very close to that calculated for the Pb(II)- $\beta$ -CD complex ( $D = 1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) [12].

## CONCLUSION

Under conditions of ligand excess, in alkaline solutions (pH > 11) Cd(II) ions form a complex with a  $\beta$ -cyclodextrin anion. The results of the polarographic investigations showed formation of a Cd $\beta$ -CD(OH)<sub>2</sub><sup>2-</sup> hydroxycomplex, the logarithm of the stability constant being  $10.4 \pm 0.1$  and the diffusion coefficient value equal to  $1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

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## References

1. Y. Matsui, T. Kurita and Y. Date, *Bull. Chem. Soc. Japan*, **45**, 3229 (1972).
2. Y. Matsui, T. Kurita, M. Yagi, T. Okayama, K. Mochida and Y. Date, *Bull. Chem. Soc. Japan*, **48**, 2187 (1975).
3. K. Mochida and Y. Matsui, *Chem. Lett.*, 963 (1976).
4. Y. Matsui and K. Kinugawa, *Bull. Chem. Soc. Japan*, **58**, 2981 (1985).
5. R. Fuchs, N. Habermann and P. Klüfers, *Angew. Chem. Int. Ed. Engl.*, **32**, 852 (1993).
6. P. K. Bose and P. L. Polavarapu, *Carbohydr. Res.*, **323**, 63 (2000).
7. M. Darj and E. R. Malinowski, *Appl. Spectrosc.*, **56**, 257 (2002).
8. B. U. Nair and G. C. Dismukes, *J. Am. Chem. Soc.*, **105**, 124 (1983).
9. N. R. Russel and M. McNamara, *J. Incl. Phen. Molec. Recogn. Chem.*, **7**, 455 (1989).
10. M. McNamara and N. R. Russel, *J. Incl. Phen. Molec. Recogn. Chem.*, **10**, 485 (1991).
11. K. Yamanari, M. Nakamichi and Y. Shimura, *Inorg. Chem.*, **28**, 248 (1989).
12. E. Norkus, G. Grincienė and R. Vaitkus, *Carbohydr. Res.*, **337**, 1657 (2002).
13. M. Ben Ali, R. Kalfat, H. Ben Quada, J. M. Chovelon and N. Jaffrezik-Renault, *Materials Science Engineering, C: Biomimetic Materials, Sensors and Systems*, **C6**, 53 (1998).
14. R. Kalfat, M. Ben Ali, R. Mlika, F. Fekih-Romdhane and N. Jaffrezik-Renault, *Int. J. Inorg. Mater.*, **2**, 225 (2000).
15. M. Ben Ali, R. Kalfat, H. Sfihi, J. M. Chovelon, H. B. Quada and N. Jaffrezik-Renault, *Sensors Actuators, B: Chemical*, **B6**, 233 (2000).
16. M. Goledzinowski, *J. Electroanal. Chem.*, **267**, 171 (1989).
17. E. Norkus, G. Grincienė and R. Vaitkus, *Chemija (Vilnius)*, **13**, 11 (2002).
18. E. Norkus and A. Vaškėlis, *Polyhedron*, **13**, 3041 (1994).
19. E. Norkus, A. Vaškėlis, I. Žakaitė and J. Reklaitis, *Talanta*, **42**, 1701 (1995).
20. E. Norkus, A. Vaškėlis and I. Žakaitė, *Talanta*, **43**, 465 (1996).
21. E. Norkus and R. Pauliukaitė, *Polish. J. Chem.*, **74**, 1231 (2000).
22. S. Li and W. C. Purdy, *Chem. Rev.*, **92**, 1457 (1992).
23. J. Szejtli, *Chem. Rev.*, **98**, 1743 (1998).
24. E. Norkus, G. Grincienė, E. Butkus and R. Vaitkus, *Chemija (Vilnius)*, **14**, 3 (2003).
25. E. Norkus, A. Vaškėlis and J. Reklaitis, *Koord. Khim.*, **14**, 325 (1988).
26. E. Norkus, A. Vaškėlis, R. Vaitkus and J. Reklaitis, *Inorg. Biochem.*, **60**, 299 (1995).
27. E. Norkus, A. Vaškėlis and J. Reklaitis, *Zh. Neorg. Khim.*, **31**, 2318 (1986).
28. E. Norkus, J. Vaičiūnienė, J. Reklaitis, E. Gaidamauskas and D. C. Crans, *Chemija (Vilnius)*, **13**, 119 (2002).
29. E. Norkus, J. Vaičiūnienė, J. Reklaitis, E. Gaidamauskas and D. C. Crans, *Chemija (Vilnius)*, **13**, 129 (2002).
30. E. Gaidamauskas, E. Norkus, E. Butkus and D. C. Crans, *to be published*.

E. Norkus, G. Grincienė, E. Butkus, R. Vaitkus

## KADMIO(II)- $\beta$ -CIKLODEKSTRINO KOMPLEKSO SUSIDARYMAS ŠARMINIUOSE TIRPALUOSE

### S a n t r a u k a

Nuolatinės srovės poliarografijos metodu tiriant Cd(II) jonų elgseną šarminiuose  $\beta$ -ciklodekstrino (CD) tirpaluose (pH > 11; 20°C,  $I = 1,0$ ), nustatyta, kad susidaro Cd $\beta$ -CD(OH)<sub>2</sub><sup>2-</sup> kompleksas. Šio komplekso patvarumo konstantos logaritmas yra  $10,4 \pm 0,1$  ir difuzijos koeficientas  $D = 1,0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .