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The Adsorption and the Influence of Modified β-Cyclodextrins on the Kinetics of Several Electrode Reactions[*]

by D. Trzciński, W. Kośnik, J. Stroka[**] and A. Temeriusz

University of Warsaw, Department of Chemistry, Pasteura 1, 02093 Warsaw, Poland

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The adsorption of modified β-cyclodextrins (β-CD) on the mercury electrode was investigated in $NaClO_4$ solutions using differential capacity measurements. The investigated cyclodextrins revealed stronger affinity towards mercury electrodes than native β-CD. Their behaviour was typical for a monolayer and consistent with that predicted by the Frumkin isotherm. The electrode kinetics of $Cu^{2+}/Cu(Hg)$ and $Cd^{2+}/Cd(Hg)$ couples was significantly inhibited in the presence of modified β-CD in the solutions while much faster in surfactant free solutions the electrode process of $Tl^{+}/Tl(Hg)$ system remained reversible also in the presence of CD's.

Key words: adsorption of modified β-cyclodextrins, electrode kinetics, inhibition of the electrode reactions

β-Cyclodextrin (β-CD) is a cyclic oligosaccharide comprising of seven D-glucopyranose residues linked *via* α-(1,4) bonds. It forms truncated con-shaped structure with relatively hydrophobic cavity and relatively hydrophilic surface, the latter is due to the presence of hydroxyl groups. It has a high dipole moment due to the presence of seven primary and fourteen secondary hydroxyl groups, located at the opposite sides of β-CD cavity. Chemical modification of hydroxyl groups in positions 2-, 3- and 6- results in CDs different properties. The most important property of CDs is their ability to form inclusion complexes with organic compounds [1–3] and inorganic anions [4,5].

A number of authors have reported adsorption of native β-CD on mercury [6–9] and solid gold electrodes [10,11]. Surface tension [6,8] and differential capacitance [6,7,9] measurements have proved strong adsorption of β-CD on mercury electrodes. The shape of differential capacity curves obtained in Na_2SO_4 solution was different from that observed in the presence of ClO_4^- ions [6,7]. For instance, large reorientation peaks of the adsorbed β-CD molecules were observed at the potentials of –0.22 V and *ca.* –0.50 V. However, the capacity curves in the presence of β-CD in both electrolytes do not point on the phase transition within the adsorbed layer. Pospišil [9] has

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

[**] Author for correspondence; e-mail: Jadwiga@chem.uw.edu.pl

reported a multilayer behaviour of the adsorbed β-CD at long experimental timescales. The adsorption of β-CD on mercury and gold electrodes was described using the Langmuir isotherm [6–8]. The adsorption coefficient β was higher in Na_2SO_4 than in $NaClO_4$ solutions [8]. Ohira and co-workers [11], using the STM method, have observed the self-organization of adsorbed the β-CD on the Au(111) electrode resulting in a "nanotube" structure. The ordered structure was formed only in the potential range from –0.45 V to –0.25 V. The effect of CD adsorption on the electrode kinetics was studied by Yamguchi *et al.* [12], Golędzinowski [13] and Hromadowa [14]. Yamaguchi *et al.* [12] observed inhibition of the first polarographic oxygen wave by α-CD and β-CD. Golędzinowski [13] studied the influence of α-CD, β-CD and γ-CD adsorption on the kinetics of electrode processes of the Cu^{2+}/Cu(Hg), Cd^{2+}/Cd(Hg) and Eu^{3+}/Eu^{2+} systems. The inhibition was most effective in the case of the Cu^{2+}/Cu(Hg) system in Na_2SO_4 solutions and dependent on the type of cyclodextrin. Inhibition coefficient k_s^{in}/k_s increased in the series α-CD < γ-CD < β-CD.

Hromadova and de Levi [14] investigated the influence of α-CD adsorption on the kinetics of Tl^+/Tl(Hg), Zn^{2+}/Zn(Hg), Pb^{2+}/Pb(Hg) and Cd^{2+}/Cd(Hg) couples in $NaClO_4$ and Na_2SO_4 solutions. They observed that adsorption of α-CD on mercury electrodes resulted in the formation of several condensed phases, depending on the anions and cations of the electrolyte used. At a low charge density, the electrode was covered by condensed film of α-CD. In the presence of sodium ions condensed film containing α-CD and Na(I) was formed at a negatively charged electrode. They reported also that the electroreduction of Tl(I) and Pb(II) remained diffusion controlled process, while reduction of Cd(II) and Zn(II) was affected by the presence of α-CD films.

In the surface studies of typical cyclodextrins with –OH groups, their interactions *via* hydrogen bonding could complicate their interfacial behaviour and affect the electrode processes which occur in this region. The differential capacity – potential plots observed in different solutions may be influenced not only by potentials and ions of the background electrolyte, but also by the hydrogen bonding which may results in the formation of various structures on the electrode surface.

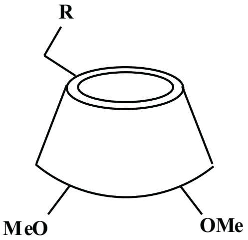
In this work modified cyclodextrins (Scheme 1) in which the hydrogen of –OH groups substituted with methyl groups were used to avoid the formation of hydrogen bonding. The surface properties of these compounds at the mercury electrode were investigated. The influence of their adsorption on the kinetics of Tl^+/Tl(Hg), Cu^{2+}/Cu(Hg) and Cd^{2+}/Cd(Hg) systems in $NaClO_4$ solutions was also studied.

EXPERIMENTAL

Differential capacitance plots were obtained using AC voltammetry with AC signal frequency of 1000 Hz. The equipment was tested and calibrated in 0.50 M $NaClO_4$ aqueous solutions. The shape of the obtained capacitance-potential dependence was in good agreement with the literature data [15].

The electrode kinetics was investigated using cyclic voltammetry (CV), and voltocoulometry. Voltocoulometric measurements were carried out using a home made apparatus with the current integration

Scheme 1



R = OMe *per*(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TM-β-CD)
R = OH *per*(2,3-di-*O*-methyl)-β-cyclodextrin (DM-β-CD)
R = NH_2 *per*(6-amino-2,3-di-*O*-methyl)-β-cyclodextrin (AM-DM-β-CD)

times in the range from 4 to 100 ms in 10 steps. The cyclic voltammetric and AC voltammetry measurements were carried out using a CH Instrument (Cordova, TN), model 660 electrochemical analyser.

Kinetic parameters of the studied processes were estimated from the voltocoulometric charge-potential Q-E curves. The estimation was based on the works of Koutecky [16], Randles [17] and Kimmerle and Chevalet [18]. Cyclic voltammetric curves of quasi-reversible processes were analysed using the Nicholson equation [19] and irreversible ones using the equation describing the peak current potential [19].

For electrochemical studies a three-electrode water-jacketed cell (25±0.1°C) was employed. Static mercury drop electrode (Laboratorni Pristroje, Prague) was used as a working electrode, and a platinum foil (2 cm^2) served as a counter electrode. All potentials were measured against the saturated (NaCl) calomel electrode (SSCE).

All chemicals used were of p.a. grade. Methylated cyclodextrins *per*(2,3-di-*O*-methyl)-β-cyclodextrin (DM-β-CD), *per*(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TM-β-CD) and *per*(6-amino-6-deoxy-2,3-di-*O*-methyl)-β-cyclodextrin (AM-DM-β-CD) were synthesized using the procedures described in [20–22] respectively. Doubly distilled and deionised water (Mili-Q, Millipore, Austria) was used for the preparation of the solutions.

RESULTS AND DISCUSSION

1. Adsorption of methylated β-cyclodextrins on mercury electrodes. Adsorption of methylated β-cyclodextrins was studied in Britton-Robinson buffered solutions (pH = 7) with 0.5 M $NaClO_4$ as a background electrolyte and different concentrations of CDs. The changes in capacitance of static mercury electrode were observed even for micromolar concentrations of CD. It was necessary to equilibrate the electrode in the solution for a relatively long time before measurements to obtain reliable and reproducible results. The results described in the present paper were found to be independent of the time of equilibration for times longer than 4 s. Occasionally for the concentration range of 10^{-5} M CDs the electrode was polarized cyclically. The direction of polarization had no influence on the capacitance.

The obtained capacitance curves for TM-β-CD, DM-β-CD and AM-DM-β-CD are presented in Figs. 1 A, B and C respectively. From the obtained data we can see that the substitution of –OH group in β-cyclodextrin by $-OCH_3$ changes its surface behaviour. For all investigated CDs starting with concentrations in μM range a decrease in differential capacity of the mercury electrode is observed. Full coverage of

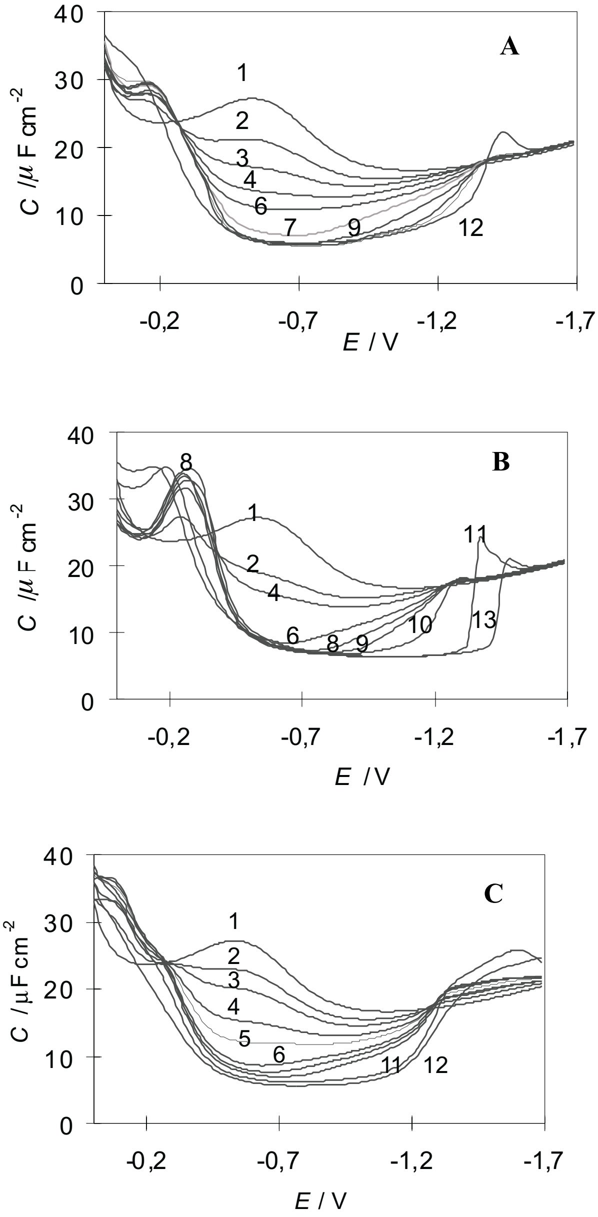


Figure 1. Differential capacity-potential curves of Hg electrode in the presence of: A – TM-β-CD, B-DM-β-CD and C-AM-DM-β-CD with concentrations equal to: 1 – 0, 2 – 1×10^{-6}, 3 – 1.5×10^{-6}, 4 – 2×10^{-6}, 5 – 2.5×10^{-6}, 6 – 3×10^{-6}, 7 – 3.5×10^{-6}, 8 – 4×10^{-6}, 9 – 5×10^{-6}, 10 – 8×10^{-6}, 11 – 1×10^{-5}, 12 – 1×10^{-4} and 13 – 2×10^{-4} M. Supporting electrolyte 0.5 M $NaClO_4$ and Britton-Robinson buffer at pH = 7.

the electrode surface was obtained at the concentrations around 10^{-4} M. The capacity decreased corresponding to the full coverage is similar for all studied Cds. The shapes of the obtained capacity curves differ from those observed for native β-CD [6–8] but are very similar to those observed for the adsorption of higher alcohols [23]. For all investigated cyclodextrins of the concentrations ranging from 0 to 10^{-5} M the capacity decreased in the potential range from –0.3 to –1.10 V. The increase of CDs concentration caused more wide potential range of adsorption and futher decrease of the capacitance. On the differential capacitance-potential curves recorded in the presence of DM-β-CD (Fig. 1B) and TM-β-CD (Fig. 1A) the adsorption-desorption peaks at potentials –1.30 and –1.40 V and reorientation peak at potential about –0.20 V were observed. For AM-DM-β-CD (Fig. 1C) in solutions of pH = 7 two humps on capacitance curves at potentials –0.075 V and –0.30 V and a broad peak at negative potentials close to –1.30 V were recorded.

The adsorption of AM-DM-β-CD from 3×10^{-6} M solutions with pH changed from 1.4 to 12 was also investigated. In the solutions of pH > 7 reorientations peaks appeared at potential about –0.30 V, while at more negative potentials adsorption-desorption peaks did not appear. In contrast in acidic solution (pH ≤ 5) the adsorption-desorption peak at potential –1.30 V was formed. It could be assigned to the protonation of $-NH_2$ groups of AM-DM-β-CD molecules.

To estimate pK_a of AM-DM-β-CD we have analysed the change of differential capacitance with pH measured in the solutions with constant AM-DM-β-CD concentration at constant potential equal to E = –0.40 V (see Fig. 2). The estimated pK_a value was equal to 9.75.

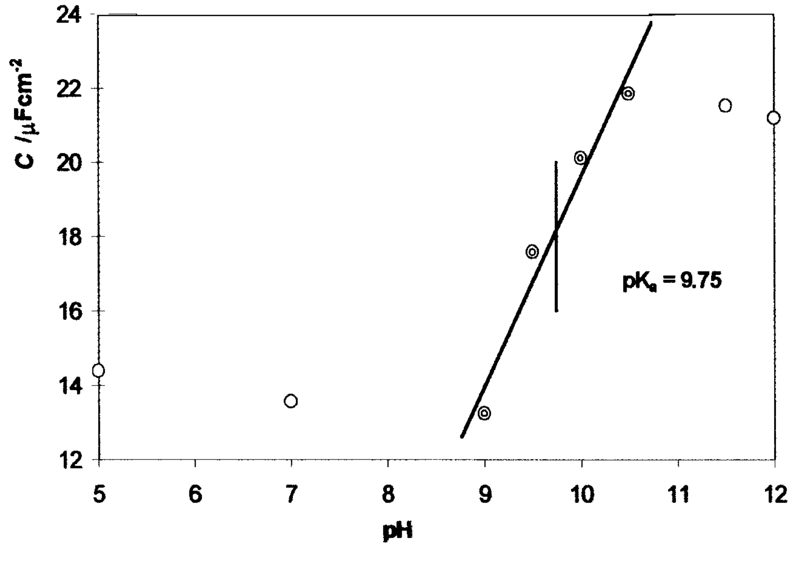


Figure 2. The dependence of differential capacity on the pH of the solution of 3×10^{-6} M AM-DM-β-CD in 0.5 M $NaClO_4$ and Britton-Robinson buffer at pH = 7.

For all investigated CDs no discontinuities on the differential capacity-potential curves were observed. The obtained results were typical fot the mercury electrode covered by a monolayer of methylated CD. Minima of differential capacitance, C_{min} slightly depended on the type of investigated CDs, and equal to 5.6 μF/cm^2 for AM-DM-β-CD and TM-β-CD, and 6.7 μF/cm^2 for DM-β-CD. Such low C_{min} values may suggest that in the potential range from –0.60 to –0.8 V the adsorbed CDs molecules have the cavities perpendicularly oriented to the mercury electrode surface. For the molecules of DM-β-CD and AM-DM-β-CD secondary methylated hydroxyl groups are in contact with the electrode surface. For TM-β-CD molecules the same orientation is also probable.

At more negative and more positive potentials, with respect to the maximum adsorption potential, differential capacity increases and the orientation of the adsorbed methylated CDs molecules becomes intermediate between the perpendicular and parallel orientation.

It follows from the literature data [6–8] that for native β-CD the reorientation peak is observed at –0.55 V and –0.20 V in solutions of 1 M $NaClO_4$ [13] or 0.5 M Na_2SO_4 respectively [7,13]. However in 0.5 M $NaClO_4$ solution in the presence of DM-β-CD or TM-β-CD the reorientation peak at potentials about –0.30 V was observed. In the solutions containing AM-DM-β-CD this peak was rather small. These results indicate that the interactions of methylated β-CD with ClO_4^- ions is weaker than that of native β-CD [7,13].

The differential capacity data for methylated β-CD shown in Figs. 1A, B and C were used to calculate the surface coverage θ from the equation:

$$\theta = \frac{C_{\theta=0} - C_{\theta}}{C_{\theta=0} - C_{\theta=1}} \qquad (1)$$

where C_{θ}, $C_{\theta=1}$ and $C_{\theta=0}$ stand for capacities of the electrode with the coverage degree equal to θ, 1 and 0 respectively. θ values obtained at different concentrations of CDs were used to construct the adsorption isotherms. The obtained results for the potentials ranging from –0.60 V to –1.00 V were fitted to the Frumkin isotherm (see Fig. 3).

$$\beta c = \frac{\theta}{1-\theta}\exp(-2a\theta) \qquad (2)$$

where β is the adsorption coefficient and a is the interaction parameter.

The dependencies of $\ln\theta/(1-\theta)c$ *vs.* θ were linear with the correlation coefficients equal to 0.998 for AM-DM-β-CD and TM-β-CD and 0.92–0.98 for DM-β-CD. Adsorption coefficients obtained at various potentials were used to calculate the Gibbs energy of adsorption:

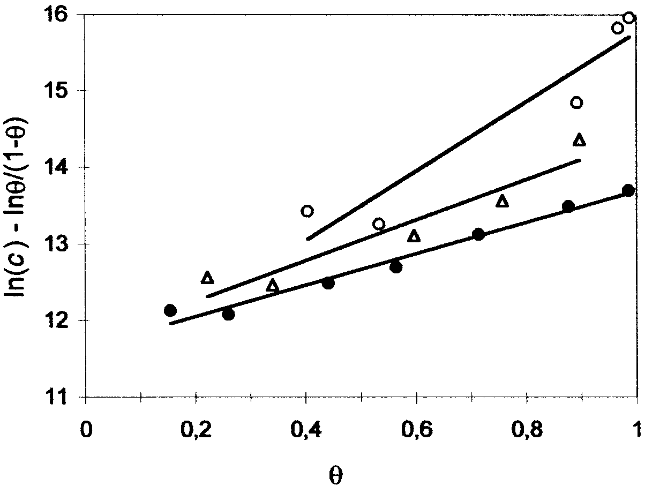


Figure 3. The fitting of the experimental data to the Frumkin isotherm for DM-β-CD adsorbed on mercury in the solutions containing 0.5 M $NaClO_4$ and Britton-Robinson buffer (pH = 7), at constant potential: –1.00 V – •, –0.90 V – Δ, and –0.70 V – o.

$$\Delta G_0 = -RT \ln(55.5\beta) \tag{3}$$

Standard data were the unit mol fraction of CDs in the solutions and unit degree of coverage in the monolayer. For DM-β-CD $-\Delta G_0$ values were plotted *vs.* the electrode potential which is shown in Fig. 4. The obtained parabolic shape is characteristic for the adsorption of non-polar organic molecules. The maximum occurs at –0.85 V which corresponds to $\beta_{max} = 1.30 \times 10^5$ dm^3 mol^{-1} and $\Delta G_0^{max} = -39.2$ kJ mol^{-1}. The obtained adsorption parameters are collected in Table 1.

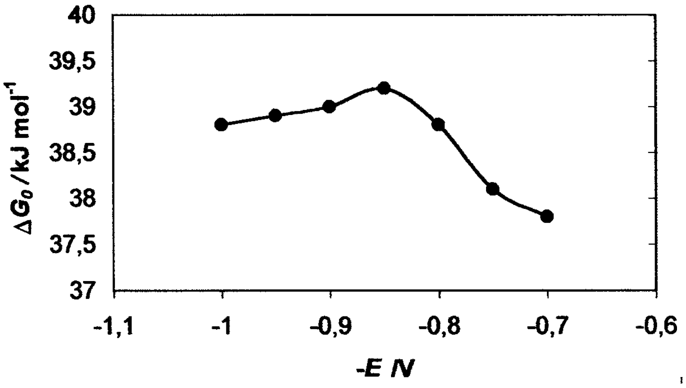


Figure 4. Gibbs energy of adsorption *vs.* potential relationship for DM-β-CD in the solution of 0.5 M $NaClO_4$ and Britton-Robinson buffer at pH = 7.

Table 1. Adsorption parameters of cyclodextrins adsorbed on the mercury electrodes in 0.5 M $NaClO_4$ solution and Britton-Robinson buffer at pH = 7.

Parameter	DM-β-CD	TM-β-CD	AM-DM-β-CD
β/dm^3/mol	$7.4\times10^4 \div 1.3\times10^5$ nonmonotonical change	$(2.0\pm0.05)\times10^5$	$(1.3\pm0.1)\times10^5$
ΔG_0/kJ/mol	$-37.8 \div -39.2$ nonmonotonical change	-40.1 ± 0.1	-38.7 ± 0.2
a	$2.3 \div 1.0$	$1.2 \div 0.9$	$1.2 \div 1.3$

The adsorption coefficient β increase in order DM-β-CD < AM-DM-β-CD < TM-β-CD, and is about 100–300 times higher than that observed for native β-CD [8] in $NaClO_4$ solutions. Apparently β-CDs are stronger adsorbed on mercury electrode than the unmodified β-CD. Interaction parameter, a, was found to be close to 1. Only for DM-β-CD it changed from 1 to 2.3, and increased linearly with the increase of the electrode potential.

2. Kinetics of the selected electrode reactions in 0.5 M NaClO4 at pH = 7, in the presence of methylated CDs. The influence of the adsorbed methylated β-CDs on the electrode kinetics of reduction of Tl(I), Cd(II) and Cu(II) ions on mercury electrodes has been investigated.

Tl^+/Tl(Hg) electrode system. Fig. 5 shows cyclic voltammetric curves for the Tl^+/Tl(Hg) system in the presence of cyclodextrin. In the potential range from 0.0 to –1.60 V only one anodic peak at the potential about –0.43 V and one cathodic peak at the potential about –0.49 V is observed. These peaks correspond to the electrode process of the Tl^+/Tl(Hg) system. At the potentials close to –1.40 V additional small peak is formed, which refers to the adsorption-desorption of cyclodextrin. The peak potentials and the formal potential are similar in the absence [24] and the presence of the all investigated adsorbed cyclodextrins. Formal potential is equal to –0.464±0.002 V. The difference between anodic and cathodic peak potentials, for all used scan rates, was equal to 60±2 mV. This indicates that Tl(I) is reversibly reduced at the mercury elec-

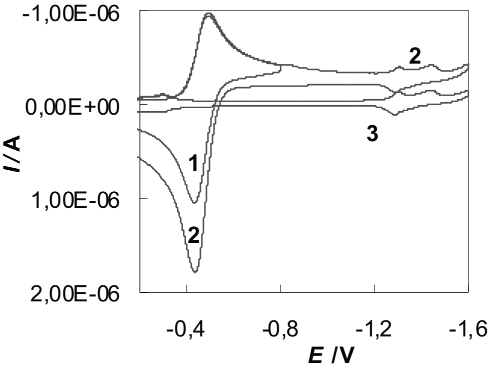


Figure 5. Cyclic voltammograms of Tl(I) (curves 1 and 2) and DM-β-CD (curve 3) in 0.5 M $NaClO_4$, Britton-Robinson buffer at pH = 7. Curve 1 – 2×10^{-4} M Tl(I), 2 – 2×10^{-4} M Tl(I) + 1×10^{-4} M DM-β-CD and curve 3 – 1×10^{-4} M DM-β-CD; v = 0.1 V s^{-1}.

trode. Even for full coverage of the electrode by adsorbed cyclodextrins the inhibition of Tl(I) electroreduction was not observed. Probably this electrode process is too fast for experimental method used, since the standard rate constant for the Tl^{+}/Tl(Hg) couple in aqueous solution is equal to 2 cm s^{-1} [24].

Cd^{2+}/Cd(Hg) system. The influence of the adsorbed DM-*β*-CD molecules on the cyclic voltammetric curves of the Cd^{2+}/Cd(Hg) system is shown in Fig. 6. In the presence of the adsorbed cyclodextrin the electrode process becomes irreversible, the current peaks are lowered, and the formal potential is slightly shifted to more negative values. The influence of TM-*β*-CD on this electrode process is very similar.

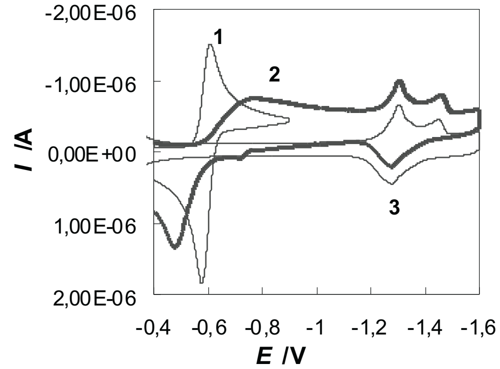


Figure 6. Cyclic voltammograms of Cd(II) (curves 1 and 2) and DM-β-CD (curve 3) in 0.5 M $NaClO_4$, Britton-Robinson buffer at pH = 7. Curve 1 – 2× 10^{-4} M Cd(II), *v* = 0.1 V s^{-1}, 2 – 2× 10^{-4} M Cd(II) + 1 × 10^{-4} M DM-*β*-CD *v*= 0.5 V s^{-1}, and curve 3 – 1 × 10^{-4}M DM-*β*-CD, *v*= 0.5 V s^{-1}.

In the presence of the adsorbed AM-DM-*β*-CD (see Fig. 7) the cathodic part of cyclic voltammograms becomes more complex. The peak (I) at –0.63 V corresponding to the Cd(II) electroreduction is very low, while at the potential around –1.15 V a new broad peak(II) is observed. This peak probably refers to electroreduction of Cd(II) ions which cannot fully react on the covered electrode. At more negative potential, a small cathodic and anodic peaks were also observed. They correspond to desorption of CD, since they were also observed in the absence of Cd(II) ions in the solution.

To elucidate the character of the peaks at potentials –0.63 and –1.15 V, 10^{-4} M Cd(II) solutions were titrated with 10^{-4} M Cd(II) and 5× 10^{-4}AM-DM-*β*-CD solution of pH = 7. During the titration the concentration ratio [AM-DM-*β*-CD]/[Cd(II)] was changed from 0 to 5. With the increase of cyclodextrin concentration the height of peak(I) at –0.630 V decreased while that of the peak at –1.15 V increased and was shifted to more negative potentials. The dependence of the peak(I) current *vs*. the concentration ratio [AM-DM-*β*-CD]/[Cd(II)] is presented in Fig. 8. This dependence may formally suggest that for 0 < [AM-DM-*β*-CD]/[Cd(II)] < 0.4, CD–Cd(II) a complex of 1:3 stoichiometry may be formed, while for higher concentrations of AM-DM-*β*-CD the complexes of 1:1 and 2:1 stoichiometry are generated.

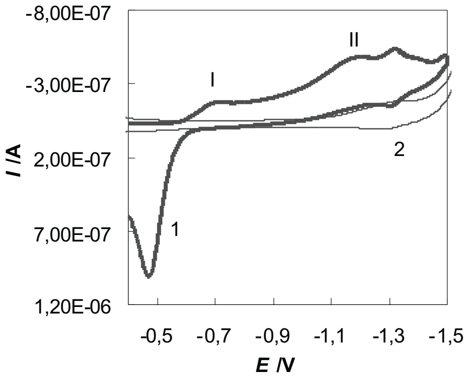


Figure 7. Cyclic voltammograms of Cd(II) (curve 1) and AM-DM-β-CD (curve 2) in 0.5 M $NaClO_4$, Britton-Robinson buffer at pH = 7; curve 1 – 2×10^{-4} M Cd(II) + 1×10^{-4} M AM-DM-β-CD and curve 2 – 1×10^{-4} M AM-DM-β-CD, $v = 0.1$ V s^{-1}.

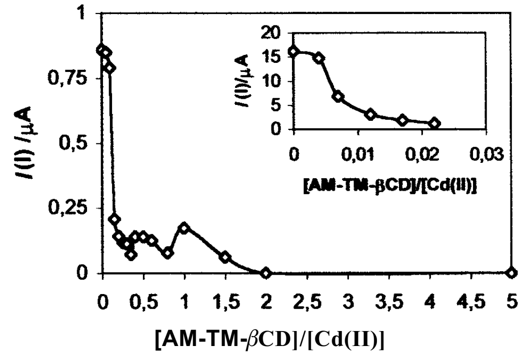


Figure 8. Cathodic peak(I) of electroreduction of Cd(II) in the solutions containing 1×10^{-4} M Cd(II) and different concentrations ratio of [AM-DM-β-CD]/[Cd(II). Supporting electrolyte 0.5 M $NaClO_4$ and Britton-Robinson buffer at pH = 7, $v = 0.1$ V s^{-1}.

Inset

Cathodic peak(I) of electroreduction of Cd(II) in the solutions with 2×10^{-3} M Cd(II) and different concentration ratio of [AM-DM-β-CD]/[Cd(II). Supporting electrolyte 0.5 M $NaClO_4$ and Britton-Robinson buffer at pH = 4.5, $v = 0.1$ V s^{-1}.

In our opinion the formation of the complex of the stochiometry 1:3 is not possible. Therefore the unusual change of the cathodic peak height with cyclodextrin concentration can be caused by the strong inhibition of Cd(II) electroreduction. To confirm this conclusion we have added, drop by drop solution of AM-DM-β-CD to 2×10^{-3} M Cd(II) solution. The concentration ratio [AM-DM-β-CD]/[Cd(II)] was then changed from 0 to 0.022. The obtained titration curves are presented in the inset of Fig. 8. The presented data show that the current of the peak(I) is strongly decreased after the [AM-DM-β-CD]/[Cd(II) ratio reaches the value 0.007. At this ratio the AM-DM-β-CD concentration is equal to 1.4×10^{-5} M. The mercury electrode is then strongly covered by the adsorbed cyclodextrin (see Fig. 1C).

The kinetic parameters of the Cd^{2+}/Cd(Hg) system in the presence of investigated cyclodextrins were calculated using the equation for irreversible process [19]. The results are given in Table 2. Obviously in the presence of methylated β-CD the electrode reaction rate of the Cd^{2+}/Cd(Hg) system decreases in the order DM-β-CD >TM-β-CD > AM-DM-β-CD and is about two orders of magnitude lower that the value observed in aqueous solution without CDs [25].

Table 2. Kinetic parameters of the Cd^{2+}/Cd(Hg) system in the solution containing 2×10^{-4} M Cd(II), 1×10^{-4} M methylated β-CD, 0.5 M $NaClO_4$ and Britton-Robinson buffer at pH = 7.

Inhibitor	E_f [V]	k_s [cm s^{-1}]	αn	k_s^{in}/k_s
DM-β-CD	–0.625±0.005	$(1.3\pm0.2)\times10^{-3}$	0.5±0.02	7.2×10^{-3}
TM-β-CD	–0.605±0.005	$(1.2\pm0.2)\times10^{-3}$	0.5±0.02	6.7×10^{-3}
AM-DM-β-CD	–0.595±0.005	$(0.96\pm0.2)\times10^{-3}$	0.5±0.03	5.3×10^{-3}
β-CD^A	–0.600	2.2×10^{-3}	0.48	3.6×10^{-2}

A – literature data in 0.5 M Na_2SO_4 solutions at pH = 2 [13].
Standard rate constant k_s for Cd^{2+}/Cd(Hg) system in the absence of inhibitor equals to 0.18 cm s^{-1} in 1 M $NaClO_4$ [25] and 0.06 cm s^{-1} in 0.5 M Na_2SO_4 solutions [28].

The estimated cathodic transfer coefficient equals to 0.5 and is close to that obtained for Cd(II) in the presence of native β-CD [13]. It is known that in the aqueous CD free solution the cathodic transfer coefficient of Cd(II) is low [25]. The change of the transfer coefficient in the presence of the adsorbed CD suggests the change of mechanism of the cadmium electroreduction on the mercury electrode.

To measure the inhibiting effect of CDs, the inhibition coefficients k_s^{in}/k_s were calculated, using the standard rate constant in the presence (k_s^{in}) and absence (k_s) of the inhibitor. The electrode reaction of the Cd^{2+}/Cd(Hg) couple is stronger inhibited by methylated β-CD than by native β-CD [13].

Cu^{2+}/Cu(Hg) system. The kinetics of Cu^{2+} reduction at the mercury electrode in 0.5 M $NaClO_4$ solutions containing TM-β-CD, DM-β-CD or AM-DM-β-CD was also investigated. In the presence of DM-β-CD the cathodic and anodic peaks are shifted to more negative values (Fig. 9, curve 2). Formal potential equal to –0.050 V is by 50 mV more negative than that observed in the solution without DM-β-CD (Fig. 9, curve 1). The electrode process of Cu^{2+}/Cu(Hg) system in the presence of CDs is quasi-reversible because the difference of $\Delta E = E_{pA} - E_{pK}$ equals to 50 mV. Adsorption DM-β-CD causes lowering of the peak(I). Rather small inhibiting effect of CD's on Cu^{2+}/Cu(Hg) system may be attributed to the quite positive potential of this redox couple. At this potential the surface coverage of the electrode by CD's is relatively small.

The peaks observed at the potential of about –0.3 V (see Fig. 9, curves 2 and 3) are probably caused by reorientation of DM-β-CD molecules on the mercury electrode. The influence of TM-β-CD compound on the reversibility of Cu^{2+}/Cu(Hg) system is very similar. Standard rate constants were calculated using the Nicholson method [19] and are presented in Table 3.

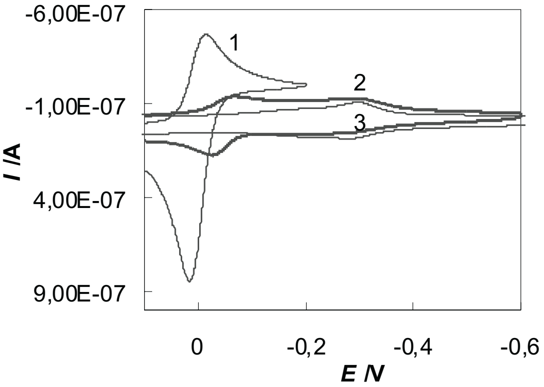


Figure 9. Cyclic voltammograms of Cu(II) (curves 1 and 2) and DM-β-CD (curve 3) in 0.5 M $NaClO_4$, Britton-Robinson buffer at pH = 7; curve 1 – 2×10^{-4} M Cu(II), $v = 0.01$ V s^{-1}, curve 2 – 2×10^{-4} M Cu(II) + 1×10^{-4} M DM-β-CD, $v = 0.1$ V s^{-1}, and curve 3 – 1×10^{-4} M DM-β-CD, $v = 0.1$ V s^{-1}.

Table 3. Kinetic parameters of the Cu^{2+}/Cu(Hg) system in the solution containing 2×10^{-4} M Cu(II), 1×10^{-4} M methylated β-CD (voltammetric measurements) or 1×10^{-4} M Cu(II), 2×10^{-4} M methylated β-CD (voltocoulometric measurements). Supporting electrolyte 0.5 M $NaClO_4$ and Britton-Robinson buffer at pH = 7.

Inhibitor	E_f [V]	k_s [cm s^{-1}]	αn	k_s^{in}/k_s
DM-β-CD	–0.05	$(1.2\pm0.2)\times10^{-3\ A}$	–	0.30
TM-β-CD	–0.05	$(1.8\pm0.02)\times10^{-3\ A}$	–	0.45
AM-DM-β-CD	0.005	$(1.1\pm0.02)\times10^{-3\ A}$	–	0.28
		$(7\pm0.6)\times10^{-3\ B,C}$	0.15 ± 0.01^{C}	
	0.020	$(2\pm0.3)\times10^{-3\ B,D}$	0.28 ± 0.01^{D}	
β-CD^{E}	0.023	1.5×10^{-4}	0.32	3.7×10^{-2}

A,B – values calculated from cyclic voltammetric and voltocoulometric curves respectively.

C,D – in the solution at pH = 7 and 8, respectively.

E – literature data obtained in 1 M $NaClO_4$ solutions of pH = 2 [13].

Standard rate constant, k_s, Cu^{2+}/Cu(Hg) system in the absence of inhibitor for equals to 4×10^{-3} cm s^{-1} [26].

In the presence of AM-DM-β-CD in the solution, the peak(I) current corresponding to electroreduction of Cu(II) to Cu(Hg) was lower. Moreover an additional peak at –0.20 V (see Fig. 10) was formed. Most probably this peak reflected the complex formation between Cu(II) cations and $-NH_2$ groups of AM-DM-β-CD molecules. To verify this hypothesis cyclic voltammograms were recorded in the solutions of the [AM-DM-β-CD]/[Cu(II)] concentration ratio being changed from 0 to 5. The cathodic peak(I) height was found to decrease with the increasing concentration of AM-DM-β-CD. However, for [AM-DM-β-CD]/[Cu(II)] = 5 the peak current did not drop to zero which rather excludes the formation of the Cu(II)-AM-DM-β-CD complex.

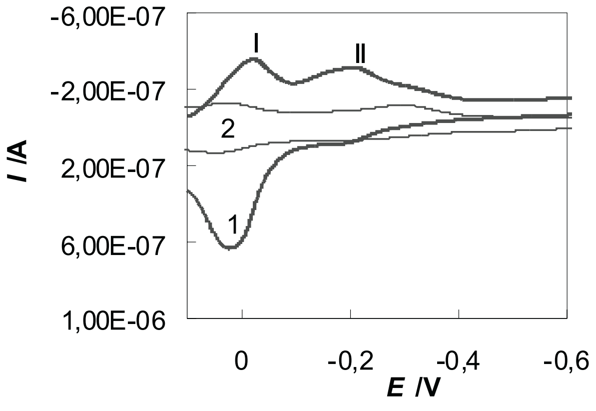


Figure 10. Cyclic voltammograms of Cu(II) (curve 1) and AM-DM-β-CD (curve 2) in 0.5 M $NaClO_4$, Britton-Robinson buffer at pH = 7: curve 1 – 2×10^{-4} M Cu(II) + 1×10^{-4} M AM-DM-β-CD, 2 – 1×10^{-4} M AM-DM-β-CD, $v = 0.1$ V s^{-1}.

The electrode process of the Cu^{2+}/Cu(Hg) system, in the presence of AM-DM-β-CD, was also studied using voltocoulometric method. Exemplary charge-potential curves are presented in Fig. 11. These dependencies (see Fig. 11, curves 1, 2 and 3) were obtained for the charge collected in the total pulse time ,Q^t, in the presence of AM-DM-β-CD. They differ in shape from the plots obtained for Cu^{2+}/Cu(Hg) system in the absence of cyclodextrin in the investigated solution. The Q^t *vs.* E plots shift to more negative potentials with the increase of pH and their slopes depend on the potential. These both effects can be assigned to the potential-induced changes in the electrode coverage with AM-DM-β-CD molecules. On the curves Q^{t-1}

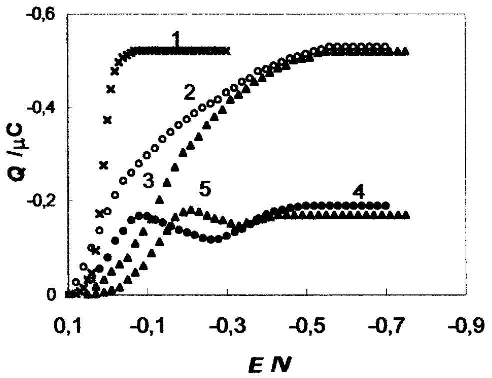


Figure 11. The charge-potential Q^t – E curves for electroreduction of 1×10^{-4} M Cu(II) (curve 1), 1×10^{-4} M Cu(II) in the presence of 2×10^{-4} M AM-DM-β-CD (curves 2 and 3) and charge-potential curves Q^{t-1}-E of 1×10^{-4} M Cu(II) in the presence of 2×10^{-4} M AM-DM-β-CD (curves 4 and 5). Supporting electrolyte 0.5 M $NaClO_4$, Britton-Robinson buffer at pH = 7 (curves 2 and 4) and at pH = 8 (curves 3 and 5). Pulse time $t_p = 49$ ms.

vs. *E,* recorded with 1 ms delay in charge collecting always a maximum was observed (see Fig. 11, curves 4 and 5). Such maximum suggests that the reagent is adsorbed at the mercury surface [27]. It can be caused by complex formation between Cu(II) cations and $-NH_2$ groups of AM-DM-β-CD molecules adsorbed on the mercury electrode. The Tafel curves were calculated from voltocoulometric Q^t-E curves. Cathodic parts of these plots were linear and described by the equations: $\log k_{fh} = -2.099-0.006\times E$, ($E$/mV) and $\log k_{fh} = -2.5548-0.006\times E$ for pH 7 and 8, respectively, with correlation coefficient equal to 0.998. The obtained standard rate constants and inhibition coefficients are given in Table 3. From the comparison of the calculated inhibition coefficients with those found for native β-CD [13] one can conclude that inhibition of the Cu^{2+}/Cu(Hg) system by methylated cyclodextrins is less effective. This is caused by weaker adsorption of methylated than native β-CD [8] at the potentials less negative than –0.30 V.

CONCLUSIONS

Methylation of hydroxyl groups of β-cyclodextrins changes the surface properties of these compounds. Adsorption of modified β-cyclodextrins is stronger than that of native β-cyclodextrin. Adsorption of DM-β-CD, TM-β-CD and AM-DM-β-CD is described by the Frumkin isotherm. The adsorption coefficient β changes from 7×10^4 to 2×10^5 dm^3 mol^{-1} in dependence on the type of cyclodextrin: DM-β-CD < AM-DM-β-CD < TM-β-CD.

The change of the kinetic parameters of the Me^{n+}/Me(Hg) systems in the presence of modified β-cyclodextrins depends on: (i) the effectiveness of adsorption of the modified CD's at the mercury electrode and (ii) the potential range of adsorption and the formal potential of reactant.

Tl(I) was reversibly reduced in the presence of modified β-cyclodextrins in the investigated solutions, because this process is very fast in the CD-free solutions.

In contrast the electroreduction of Cd(II) and Cu(II) at the mercury electrode was inhibited by the adsorbed modified β-cyclodextrins. Higher values of the k_s^{in}/k_s parameter for Cu(II)/Cu(Hg) than for the Cd(II)/Cd(Hg) can be caused by the potential differences at which the both reactions occur. It has been evidenced from differential capacity measurements (Fig. 1) that at potential electroreduction of Cd(II) the coverage of the electrode with modified β-cyclodextrins is higher than the coverage at the potential of Cu(II) electroreduction.

It has been found that only Cu(II) ions form complexes with AM-DM-β-CD molecules in the surface layer.

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