The Adsorption of α- and β-Cyclodextrins on the Dropping Mercury Electrode in an Aqueous Solution

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The adsorption of α- and β-cyclodextrins on the surface of the dropping mercury electrode was examined in a phosphate buffer solution by means of voltammetry with a triangular potential sweep. The α- and β-cyclodextrins gave two capacitive peaks corresponding to the adsorption and desorption processes respectively. The α-cyclodextrin additionally gave two cathodic peaks and an anodic peak, probably due to reorientation processes. The effects on the peak heights were investigated in terms of the sweep rate, the cyclodextrin concentration, the temperature, the ionic strength, and the pH. The adsorption of both cyclodextrins followed the Langmuir isotherm, and the equilibrium constants for the adsorption were evaluated to be 1.2×10^4 M^{-1} for α-cyclodextrin and 1.0×10^5 M^{-1} for β-cyclodextrin at 25°C and pH 6.5.

The degradation of starch by the action of *Bacillus macerans* amylase yields cyclic dextrins composed of six (in α-cyclodextrin), seven (in β-cyclodextrin), or more α-D-glucopyranose units linked 1→4 as in amylose.[1] These molecules have void spaces and form 1 : 1 inclusion complexes with a variety of organic compounds in aqueous solutions.[2] In the course of a polarographic study of the inclusion complexes, we found that cyclodextrins are adsorbed on the surface of a dropping mercury electrode. This phenomenon is interesting in connection not only with the analysis, but also with the physicochemical properties of cyclodextrins. The present study was undertaken in order to examine the adsorption behavior of α- and β-cyclodextrins by means of voltammetry with a triangular potential sweep. This method is suitable for obtaining both the charging and discharging capacitive curves as functions of the applied potential,[3] although the method of differential capacity measurements with an impedance-type capacity bridge is in general use for the investigation of the electric double-layer structure and the adsorption of various organic substances.[4]

Experimental

The α- and β-cyclodextrins were prepared by the method of Lane and Pirt[5] and were purified according to the directions of Cramer and Henglein.[6]

The apparatus used for the measurement of the capacity patterns was of a Randles-Sevcik type with a triangular potential sweep (multi-sweep method). The details have been described previously.[7] A two-electrode system with a dropping mercury electrode and mercury pool electrode was used. In order to minimize the iR drop yielded across the cell, a fairly concentrated electrolyte solution (0.50 M of phosphate buffer) was used, except when the effect of the buffer concentration was examined. No test solution was degassed, since it had been found that dissolved oxygen gives no capacitive peak and has no influence on the current-potential curves of the α- and β-cyclodextrins. The dropping mercury electrode used in most experiments had the following characteristics in a 0.50 M phosphate buffer (pH 6.5): $m=0.587$ mg/s and $t=11.0$ s. The capacitive current increases with an increase in the surface area of the dropping mercury electrode. The influence of the growth of the mercury drop on the current was minimized by registering the current-potential curves immediately before the drop fell. The time interval from the moment the mercury begins to form to the time of exposure of the capacity pattern was measured by means of a stopwatch.

The DC and AC polarography were carried out with a Yanagimoto polarograph, model GA-103, which has an admittance-type capacity bridge. The superimposed sinusoidal voltage was 15 mV, 60 Hz.

Results

The adsorption of organic compounds on the mercury electrode surface causes, in general, a decrease in the surface tension of the mercury. Figure 1 shows the effects of α- and β-cyclodextrins on the electrocapillary curve of the 0.50 M phosphate buffer (pH 6.5)

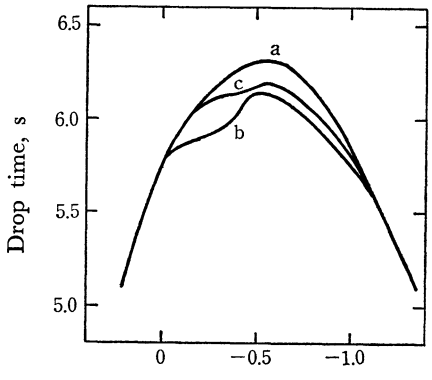

Fig. 1. Electrocapillary curves at 25 °C.
a: 0.50 M phosphate buffer (pH 6.5), b: a+5.0 mM α-cyclodextrin, c: a+5.0 mM β-cyclodextrin.

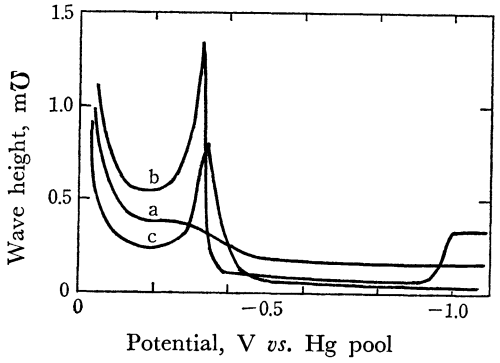

Fig. 2. AC polarograms of the cyclodextrins in 0.50 M phosphate buffer (pH 6.5) at 25 °C.
a: No cyclodextrin, b: 1.0 mM α-cyclodextrin, c: 1.0 mM β-cyclodextrin.

at 25 °C. The drop time of the mercury electrode did markedly decrease upon the addition of the cyclodextrins at potentials from 0.0 to −1.1 V *vs.* SCE for α-cyclodextrin and from −0.2 to −1.1 V *vs.* SCE for β-cyclodextrin.

Neither α- nor β-cyclodextrin gave any DC polarographic wave at these potential regions, but both did give a well-defined AC polarographic wave (Fig. 2).

Figures 3 and 4 are the current-potential curves of α- and β-cyclodextrins respectively, as determined by cyclic voltammetry. No other peaks due to the cyclodextrins were observed at any potential range not shown in these figures. A dilute solution (below 0.05 mM) of α-cyclodextrin gave two peaks (A and B) in the cathodic scan and two peaks (C and D) in the anodic scan, whereas a concentrated solution (above 0.10 mM) of the cyclodextrin gave another peak (A') on the right shoulder of the A peak. On the other hand, a solution of β-cyclodextrin gave only one cathodic peak (A) and one anodic peak (B) at all the concentrations studied (up to 1.00 mM). All the facts described above indicate that both α- and β-cyclodextrins are adsorbed on the surface of the mercury electrode and lower the differential capacity of the electrode, although the adsorption and desorption processes are not straightforward in the case of α-cyclodextrin. The potentials at which the capacitive peaks appeared are as follows (V *vs.* Hg pool): for 0.20 mM α-cyclodextrin; A, −0.44 V, A', −0.46 V, B, −1.19 V, C, −0.78 V, D, −0.36 V, for 0.01 mM β-cyclodextrin; A, −0.43 V, B, −0.37 V. The potentials of the A' and D peaks for α-cyclodextrin shifted slightly toward less negative potentials with an increase in the cyclodextrin concentration.

Since the capacitive current (i) varies in proportion to the surface area (A) of the dropping mercury electrode, the current density ($j=i/A$) was used instead of i in the following results. The value of A was calculated by means of this equation:[8]

$$A = (4\pi)^{1/3}(3mt/\rho)^{2/3} \quad (1)$$

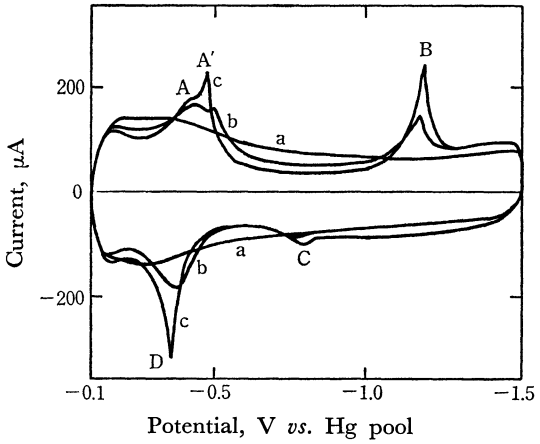

Fig. 3. Current-potential curves in the cyclic voltammetry of α-cyclodextrin in 0.50 M phosphate buffer (pH 6.5) at 25 °C.
a: 0.00 mM, b: 0.10 mM, c: 0.20 mM.
Sweep frequency: 20 Hz.

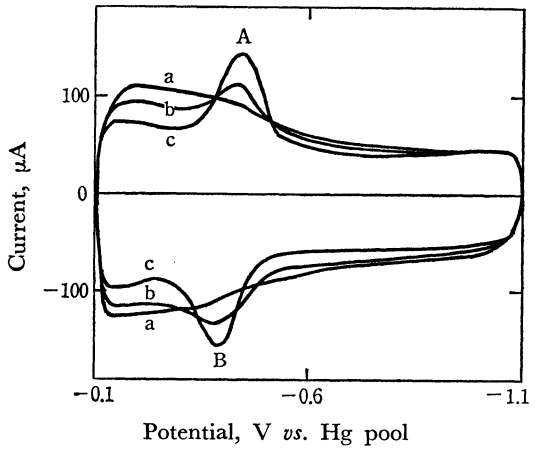

Fig. 4. Current-potential curves in cyclic voltammetry of β-cyclodextrin in 0.50 M phosphate buffer (pH 6.5) at 25 °C.
a: 0.000 mM, b: 0.005 mM, c: 0.025 mM.
Sweep frequency: 20 Hz.

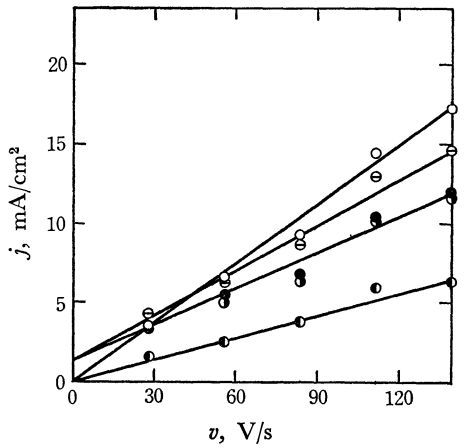

Fig. 5. The plots of j *vs.* potential sweep rate for the capacitive peaks of 0.10 mM α-cyclodextrin in 0.50 M phosphate buffer (pH 6.5) at 25 °C.
○: Peak A, ●: Peak A', ◑: Peak B, ◐: Peak C, ⊖: Peak D.

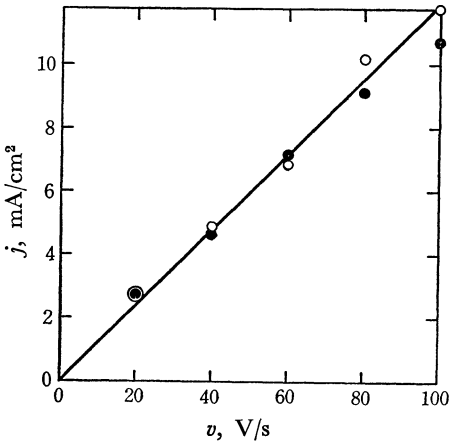

Fig. 6. The plots of j *vs.* potential sweep rate for the capacitive peaks of 0.010 mM β-cyclodextrin in 0.50 M phosphate buffer (pH 6.5) at 25 °C.
○: Peak A, ●: Peak B.

where m is the average mass of mercury flowing per unit time; t, the time interval from the moment the mercury begins to form to the time of photographic exposure, and ρ, the density of mercury. According to Loveland and Elving,[3] the value of j should be proportional to the potential sweep rate (v). Figures 5 and 6 show the plots of j *vs.* v for the 0.10 mM α- and 0.010 mM β-cyclodextrin solutions respectively in the 0.50 M phosphate buffer (pH 6.5) at 25 °C. Virtually linear plots passing the point of origin were obtained for the A and C peaks of α-cyclodextrin and for the A and B peaks of β-cyclodextrin. However, the approximately linear plots for A', B, and D peaks of α-cyclodextrin did not pass the point of origin; this suggests that these peaks involve some complex processes other than the simple adsorption-desorption processes.

Figures 7 and 8 show the plots of j *vs.* the concentrations of α- and β-cyclodextrins respectively in the 0.50 M phosphate buffer (pH 6.5) at 25 °C. Again, the plots for the A and C peaks of α-cyclodextrin and for the A and B peaks for β-cyclodextrin showed the curves characteristic of the Langmuir isotherm, but the plots for the A', B, and D peaks of α-cyclodextrin did not. On the assumption that the value of $j-j_0$ (j_0 is the value of j at a zero concentration of the adsorbate) is proportional to the amount of material adsorbed,[9] the Langmuir isotherm can be written as:

$$(j-j_0)/(j_\infty-j_0) = Kc/(1+Kc) \quad (2)$$

where j_∞ is the maximum value of j; c, the concentration of the adsorbate, and K, the equilibrium constant for the adsorption. Eq. (2) can be rewritten as:

$$j = j_\infty - (j-j_0)/Kc \quad (3)$$

Figure 9 shows the plots of j *vs.* $(j-j_0)/c$ for the A peaks of α- and β-cyclodextrins. Both of the plots are approximately linear. The K values were determined from the slopes of the plots to be 1.2×10^4 M^{-1} for α-cyclodextrin and 1.0×10^5 M^{-1} for β-cyclodextrin.

The dependence of j on the temperature is shown in Table 1. The j values for the A and C peaks of α-cyclodextrin and for the A and B peaks of β-cyclodextrin increased slightly with an increase in the

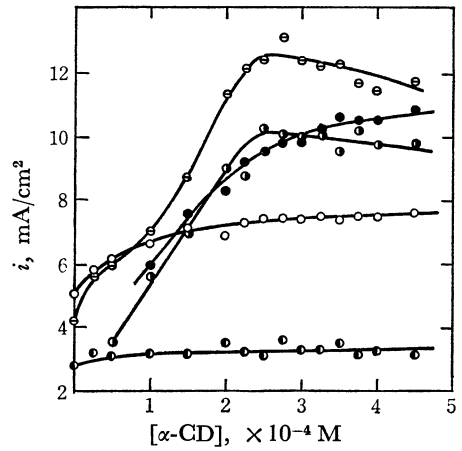

Fig. 7. The plots of j *vs.* the α-cyclodextrin concentration in 0.50 M phosphate buffer (pH 6.5) at 25 °C.
○: Peak A, ●: Peak A', ◑: Peak B, ◐: Peak C, ⊖: Peak D.
Potential sweep rate: 56 V/s.

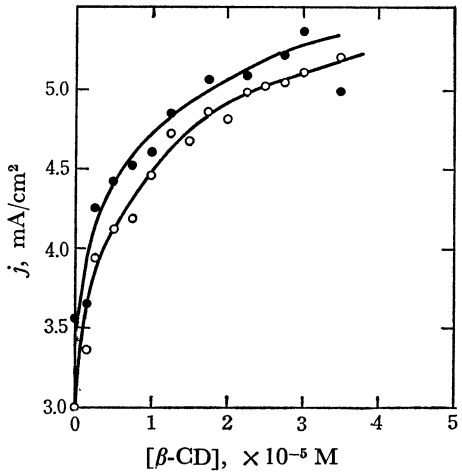

Fig. 8. The plots of j *vs.* the β-cyclodextrin concentration in 0.50 M phosphate buffer (pH 6.5) at 25 °C.
○: Peak A, ●: Peak B.
Potential sweep rate: 40 V/s.

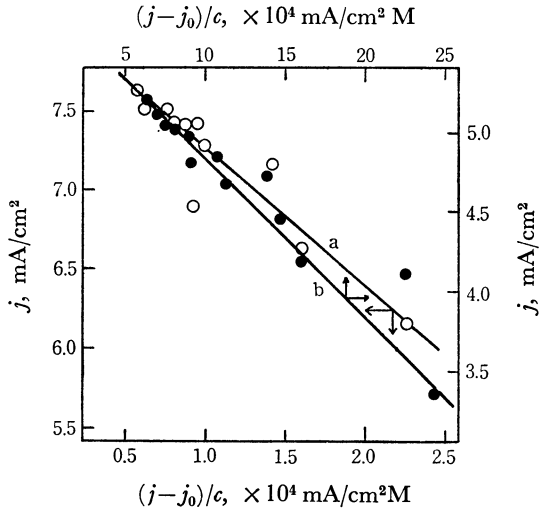

Fig. 9. The plots of j *vs.* $(j-j_0)/c$ for the A peaks of α- and β-cyclodextrins in 0.50 M phosphate buffer (pH 6.5) at 25 °C.
a: α-cyclodextrin, b: β-cyclodextrin.

Table 1. The dependence of the peak heights on temperature in 0.5 M phosphate buffer (pH 6.5)

Cyclodextrin	peak	$(1/j)(dj/dT)$, %
α[a]	A	+0.4
	A'	−2.1
	B	−1.0
	C	+0.5
	D	−0.9
β[b]	A	+0.1
	B	+0.1

a) [α-CD]=0.10 mM and v=56 V/s. b) [β-CD] = 0.010 mM and v = 40 V/s.

temperature. On the other hand, the other peaks of α-cyclodextrin were significantly lowered with a temperature increase. When the concentration of the phosphate buffer at pH 6.5 increased from 0.025 M to 0.50 M, the heights of the A and C peaks for α-cyclodextrin increased slightly, whereas that of the A′ peak decreased slightly. The other peaks of α- and β-cyclodextrins showed virtually no change with an increase in the ionic strength. A similar change in the heights for the A and A′ peaks of α-cyclodextrin was observed when the pH of the phosphate buffer (0.50 M) was increased from 5.0 to 8.0.

Discussion

The adsorption of α- and β-cyclodextrins on the surface of the dropping mercury electrode is apparent on the basis of the following observations: (1) a solution of α- or β-cyclodextrin gives no DC polarographic wave, but does give an AC polarographic peak and some cyclic voltammetric peaks, and (2) the surface tension of the dropping mercury electrode in a phosphate buffer is markedly depressed by the addition of α- or β-cyclodextrin.

There is no dobut that the least negative capacitive peak in the cathodic scan for each cyclodextrin (Peak A) corresponds to the adsorption process of the cyclodextrin. The dependence of the peak height for this process on the rate of the potential scan agrees with the equation presented for the capacitive current. The peak height also follows the Langmuir isotherm. The equilibrium constant (K) for the adsorption of β-cyclodextrin ($1.0\times10^5\ M^{-1}$) is about 8 times larger than that of α-cyclodextrin ($1.2\times10^4\ M^{-1}$). This result may be related to the fact that β-cyclodextrin is about 8 times less soluble in water than α-cyclodextrin.[10] According to Blomgren, Bockris, and Jesch,[11] the adsorptivity of organic substances on the mercury surface increases with a decrease in the solubility in water. Similar results have also been reported by Kaganovich *et al.*[12] who showed that the adsorption of normal aliphatic acids, alcohols, or amines is enhanced by increasing the length of the hydrocarbon chains—that is, by a decrease in the solubility in water.

The anodic peak B of β-cyclodextrin is almost symmetrical with the cathodic peak A and may be due to the desorption of the cyclodextrin. In the case of α-cyclodextrin, the behavior of the peaks other than the cathodic peak A is very complex. The A′ peak does not appear until the concentration of α-cyclodextrin exceeds 0.10 mM, in which case, according to the plot of j for peak A *vs.* the cyclodextrin concentration in Fig. 7, about half of the adsorption sites of the mercury electrode are occupied by the adsorbate. The peak height decreases with an increase in the temperature, the pH, or the ionic strength. The peak can be attributed either to the multilayer adsorption of the cyclodextrin or, more probably, to the reorientation of the adsorbed molecules on the electrode surface. However, it is not clear why the behavior of α-cyclodextrin is so different from that of β-cyclodextrin. The behavior of the B peak of α-cyclodextrin is similar to that of the A′ peak, so it is reasonable to ascribe the peak to the reverse process of the A′ peak. The anodic peaks C and D of α-cyclodextrin may also involve the adsorption-desorption and/or reorientation processes, but the details remain still unclear.

The present cyclic-voltammetric method could be applied to the determination of microquantities of the cyclodextrins. By the use of calibration curves, it is possible to determine *ca.* 20—200 μg/ml of α-cyclodextrin or *ca.* 1—20 μg/ml of β-cyclodextrin at 25 °C.

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